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Identity and Distribution of Residues of Energetic Compounds at Military Live-Fire Training Ranges

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ABSTRACT

Environmental stewardship of military training ranges is an important objective of the Department of Defense. Therefore, an understanding of the explosives residues resulting from military training with various weapon systems is critical to range managers. A series of field sampling experiments was conducted at 27 military firing ranges in the United States and Canada to provide information on the identity and distribution of energetic munitions constituents. Different types of ranges were studied, including hand grenade, antitank rocket, artillery, bombing, and demolition ranges. Both firing points and impact areas were studied. Energetic compounds (explosives and propellants) were determined and linked to the type of munition used and the major mechanisms of deposition. At impact areas, the largest deposition of residues of energetic compounds is due to low-order detonations, or, in some cases, munitions that split open upon impact. The major residue deposited and its distribution varies for different types of ranges based upon the composition of the high explosive present in the warheads of the rounds fired at that type of range. For antitank range impact areas, the major residue present is HMX from the octol explosive used in the M72 66-mm LAW rockets. At artillery range impact areas, the major residues are TNT and/or RDX from the military-grade TNT and Composition B used in warheads of artillery and mortar rounds. Residues are very heterogeneously distributed at artillery range impact areas and can be described as randomly distributed point sources. RDX and TNT are the major residues at hand grenade ranges and their distribution is less heterogeneous due to the large number of individual detonations in a smaller area that further disperses the residues over the surface and at shallow depths. TNT is the major energetic compound detected at bombing ranges due to its presence in tritonal, the most common explosive used in bombs. RDX is the most common energetic compound at demolition ranges due to its presence as the major component of C4 demolition explosive. NG and 2,4-DNT are also frequently detected at demolition ranges as a result of the disposal of excess propellant. Once dissolved, RDX and HMX are the most mobile of the organic energetic compounds deposited on ranges, both vertically in the soil profile and horizontally across the surface.

Results of these studies demonstrate that the potential for range contamination is specific to range activities. Large areas of training ranges are uncontaminated, while residues in smaller areas, e.g., those around targets, firing points, and low-order detonations, are potentially significant. Range managers can, therefore, limit management practices for residue control to specific areas and specific types of firing activities.

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PREFACE

This report was prepared by Dr. Thomas F. Jenkins, Alan D. Hewitt, Marianne E. Walsh, and Charles M. Collins, Environmental Sciences Branch, U.S. Army Engineer Research and Development Center (ERDC), Cold Regions Research and Engineering Laboratory (CRREL), Hanover, New Hampshire; Dr. Sonia Thiboutot, Dr. Guy Ampleman, and Dr. Sylvie Brochu, Defence R&D Canada-Valcartier, Val-Belair, Quebec, Canada; Thomas A. Ranney, Science and Technology Corporation, Hanover, New Hampshire; Charles A. Ramsey, EnviroStat, Inc., Fort Collins, Colorado; Dr. Clarence L. Grant, Professor Emeritus, University of New Hampshire, Durham, New Hampshire; Susan R. Bigl, Geophysical Sciences Branch, ERDC-CRREL; and Dr. Judith C. Pennington, ERDC Environmental Laboratory (EL), Vicksburg, Mississippi.

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The Commander and Executive Director of the Engineer Research and Development Center is Colonel James R. Rowan, EN. The Director is Dr. James R. Houston.

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1 INTRODUCTION

Over the past few years a series of field experiments has been conducted at 27 military installations in the United States and Canada (Fig. 1). The objectives of these studies have been to identify the types of energetic residues present in the surface soils at various types of military live-fire training ranges and to estimate concentrations and distributions of these residues. The concern is that these surface residues could serve as sources for off-site migration of various compounds in groundwater or surface water. Until now most of the results from these studies have been available only in U.S. and Canadian government reports for individual (occasionally several) installations. It is the objective of this report to summarize and synthesize the huge body of knowledge that has been gained from these studies. Also, research to develop approaches to remediate ranges is underway, often with an incomplete understanding of the nature of the problems to be addressed.

For the purposes of this discussion we define energetic compounds as those chemicals used in military explosives and propellants. These include 2,4,6-trinitrotoluene (TNT), 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX), and 1,3,5,7-tetrahydro-1,3,5,7-tetranitrotetrazocine (HMX), which are used as high explosives, and nitrocellulose (NC), 2,4-dinitrotoluene (DNT), nitroglycerin (NG), and nitroguanidine (NQ), which are used in gun and rocket propellants. Residues of these compounds are deposited onto surface soils, generally as particles (high explosives and propellants) or fibers and slivers (propellants) as troops conduct live-fire training.

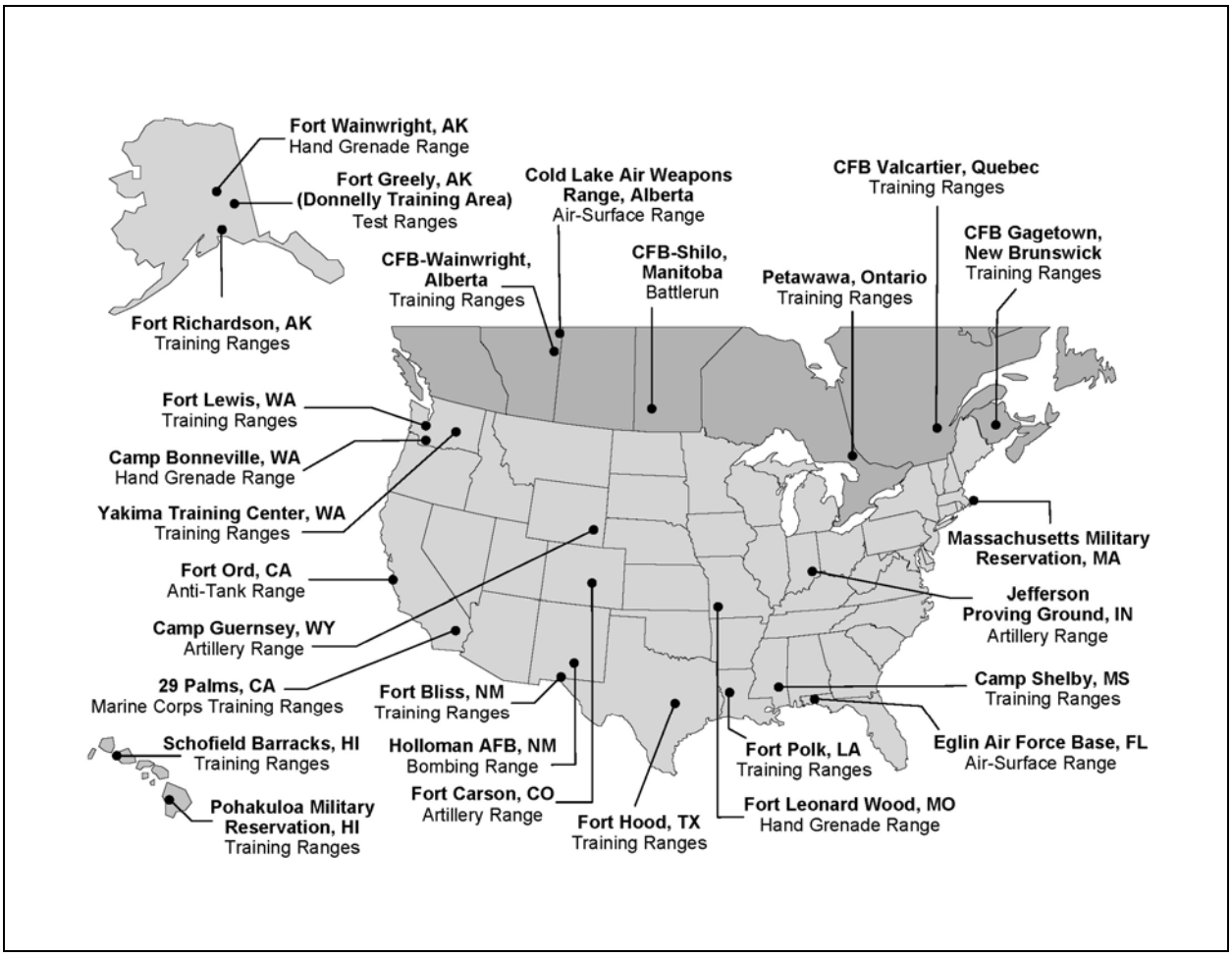


Figure 1. U.S. and Canadian installations where field experiments were conducted.

We have studied a number of different types of live-fire and demolition ranges at U.S. and Canadian military bases. These include hand grenade, rifle grenade, antitank rocket, demolition, tank firing, mortar, artillery, C-130 gunship, and bombing ranges. Training at these ranges is conducted with different types of munitions that contain a variety of energetic formulations. At many ranges, there is an area where the weapon is fired and a separate impact area where detonations occur. Generally, energetic residues at the firing points are composed of compounds used in propellant formulations, whereas residues at the impact areas are compounds used as high explosives in the munition warheads, or white phosphorus (WP) from smoke rounds.

2 METHODS

Soil sampling

Soil sampling methods for the various types of ranges have evolved as our understanding of the nature of the deposition and distribution of energetic compounds has improved. Generally, stainless steel scoops were used to sample non-cohesive soils such as sands and gravels, and specially designed corers were used in more cohesive soils such as silts and clays, and where vegetation is present (M.R. Walsh 2004). Because of the presence of unexploded ordnance (UXO) at many of these ranges, soil sampling often was limited to surface and near-surface depths. Because deposition of residues occurs as particles and fibers at the surface, this was not considered a serious limitation; furthermore, soil-profiling data indicate that the major residue concentrations are nearly always in the top few centimeters of soil.

When soil sampling was conducted to estimate the mean concentration of a compound for a given area, multi-increment composite samples were found to be essential for obtaining representative samples. This was necessitated by the high degree of spatial heterogeneity found for residues of all types of energetic compounds (M.E. Walsh et al. 1997, 2004; Jenkins et al. 1999, 2004a,b, 2005; Hewitt et al. 2005) and the excessive cost associated with analyzing very large numbers of discrete samples. The numbers of increments or mass in the sample needed to provide a reliable estimate of the mean concentration for various ranges differs depending on the nature of the residue deposition (Jenkins et al. 2004a,b, 2005; Hewitt et al. 2005; M.E. Walsh et al. 2005) and the size of the area being characterized. Generally 30 to 50 increments were found to be adequate for 10-m × 10-m (100-m^2) areas, and 50 to 100 increments were adequate for 100-m × 100-m (10,000-m^2) areas. Discrete samples were used to characterize residues near ruptured items and in areas where solid explosives were observed on the surface, or when doing near-surface depth profiling near high-concentration sources.

Sample processing and subsampling

As with sample collection, various methods of sample processing and subsampling were used during these studies as we gained more knowledge of the nature of these residue-containing soils. Because of the particulate nature of the residues, compositional heterogeneity can be a significant component of overall uncertainty (Pitard 1993). Compositional heterogeneity has been defined by Pitard (1993) as the heterogeneity that is inherent to the composition of each particle making up the sample. As a result, the sample processing methodology specified in SW846 Method 8330 (EPA 1994) was found to be inadequate in

several respects for quantitative analysis of energetic compounds in soils from training ranges. Two major changes proved necessary. The first change was to increase the sieve size used during sample processing from #30 (0.595 mm) to #10 (2 mm). For example, we found that in soils from the Fort Lewis hand grenade range, about half of the RDX mass and more than half of the TNT mass was in the size fraction greater than 0.595 mm and less than 2 mm (Table 1). Hewitt et al. (2004) and M.E. Walsh et al. (2005) reported similar findings for soils containing propellant residues. Thus, in our most recent work, we used 2-mm (10-mesh) sieves to separate oversized material from the air-dried soil (Jenkins et al. 2004a, b).

Secondly, Walsh et al. (2002) demonstrated that mechanical grinding prior to subsampling was effective at significantly reducing the subsampling relative standard deviation, sometimes by as much as two orders of magnitude. After sieving, we grind soils from impact areas for 60 sec on a Lab TechEssa LM2 (LabTech Essa Pty. Ltd., Bassendean, WA, Australia) puck mill grinder. For soils from firing points where the residues are often present as fibers, it is necessary to grind for five minutes in one-minute increments, allowing a short cooling period between grinds (M.E. Walsh et al. 2005). After grinding, samples are mixed thoroughly and spread to form a 1-cm-thick layer, and subsamples are obtained by collecting at least 30 increments randomly from the ground material to obtain a subsample mass of about 10 g (Jenkins et al. 2005).

Sample analysis

The 10-g portions of soil are extracted with 20 mL of acetonitrile using either an ultrasonic bath or shaker table for 18 hours. The extracts are then analyzed using either reversed-phase high-pressure liquid chromatography (RP-HPLC) Method 8330 (EPA 1994) or gas chromatography with electron capture detector (GC-ECD) Method 8095 (EPA 1999). Many samples were analyzed using both methods to provide increased confidence in the identity of detected analytes and to provide analytical results for various energetic compounds that can differ in concentration by several orders of magnitude within the same sample.

A few samples were analyzed by other methods such as GC/MS to identify the presence of other organics, but the main objective of this work was to determine concentrations of the energetic compounds and their major environmental transformation products. Thus, the suite of target analytes included the major nitroaromatic and nitramine high explosives used by the Army (TNT, RDX, HMX, tetryl, pentaerythritol tetranitrate [PETN], the major monomeric propellant-related compounds (NG, 2,4-DNT, 2,6-DNT), and the major environmental transformation products that are known to form in aerobic surface and

near-surface soils (1,3,5-trinitrobenzene [TNB], 2-amino-4,6-dinitrotolene [2ADNT], and 4-amino-2,6-dinitrotoluene [4ADNT]). The mono nitro compounds (nitrobenzene [NB], 2-nitrotoluene [2NT], 3-nitrotoluene [3NT], and 4-nitrotoluene [4NT]) are target analytes of Method 8330 and Method 8095 and would have been detected if present, but none were detected in soils from these ranges. In samples containing percent levels of TNT, unsymmetrical isomers of trinitrotoluene and other isomers of DNT are detectable, but no attempt was made to quantify these trace manufacturing impurities. In a recent study by Clausen et al. (2004), in which more than 15,000 soil samples from the Massachusetts Military Reservation (MMR) were analyzed, these target analytes constituted the major detectable organic compounds.

Table 1. Comparison of energetic residues in various particle size ranges for soil samples from the Fort Lewis, Washington, hand grenade range.

Sample	TNT concentration (mg/kg)			RDX concentration (mg/kg)		
	>2 mm	<2 to >0.595 mm	<0.595 mm	>2 mm	<2 to >0.595 mm	<0.595 mm
1	0.19	1.36	0.81	0.02	0.05	0.13
2	0.21	21.0	2.71	0.02	6.36	1.11
3	0.36	3.28	0.55	0.02	0.71	0.29
4	0.18	0.42	2.41	0.01	0.71	0.29
5	0.30	5.72	1.65	0.02	0.04	0.35
6	0.03	16.0	0.04	0.03	0.07	0.38
7	0.11	3.25	0.34	0.03	6.73	1.86
8	0.10	0.05	0.08	0.02	0.05	0.15
9	0.29	3.08	0.06	0.03	6.62	0.68
10	0.05	0.05	0.03	0.02	0.07	0.13
Sample	Mass of TNT (mg)*			Mass of RDX (mg)*		
	>2 mm	<2 to >0.595 mm	<0.595 mm	>2 mm	<2 to >0.595 mm	<0.595 mm
1	0.05	0.31	0.65	0.01	0.01	0.01
2	0.05	5.11	1.94	0.01	1.54	0.79
3	0.07	0.70	0.39	0.004	0.15	0.20
4	0.04	0.10	1.53	0.003	0.01	0.18
5	0.05	1.23	1.19	0.004	0.01	0.26
6	0.01	4.03	0.03	0.01	0.02	0.27
7	0.03	0.98	0.04	0.01	2.03	2.20
8	0.03	0.01	0.078	0.005	0.01	0.13
9	0.06	0.77	0.06	0.01	1.65	0.59
10	0.02	0.02	0.03	0.01	0.03	0.13

* Calculated from the concentrations of TNT and RDX times the mass of soil in the various particle size ranges.

3 RESULTS AND DISCUSSION

The types of ranges studied for each installation where field experiments were conducted are discussed in the following sections and are organized by range type. This was done because different munitions containing different energetic compounds are used at the various types of ranges, and the nature of the deposition and the resulting distribution patterns differ as well.

Hand grenade ranges

Hand grenade ranges are generally only a few hectares in size and, because of the large number of individual detonations in a small area, are poorly vegetated. These ranges often have several training bays from which soldiers throw grenades. Most of the detonation craters lie at distances between 15 and 35 m from the throwing pits. The surfaces of these ranges vary from gravels and sands to clays depending on the location. The management practices used at the various installations also vary significantly. At some ranges craters are filled in and the surface is leveled frequently; at others, the craters are left intact.

The majority of training at hand grenade ranges in the United States is with M67 fragmentation grenades, in which the explosive charge is 185 g of Composition B. In Canada, training is generally with C-13 fragmentation grenades that have the same specifications as the M67. Composition B is 60% military-grade RDX, 39% military-grade TNT, and 1% wax. Military-grade RDX contains about 90% RDX and 10% HMX. Military-grade TNT contains about 99% 2,4,6-TNT and a few tenths of a percent of other isomers of TNT and DNT (Leggett et al. 1977).

Because discrete samples in close proximity from these ranges varied by several orders of magnitude (Jenkins et al. 2001), we conducted two types of studies to improve reproducibility. First we studied the use of multi-increment samples as a means of overcoming the contribution of distributional heterogeneity. Distributional heterogeneity has been defined by Pitard (1993) as the heterogeneity that is inherent in the manner in which the particles are scattered. We conducted a study at the Fort Wainwright hand grenade range where we collected five discrete samples and five sets of replicate multi-increment samples of 5, 10, 20, and 40 increments each within a 10-m × 10-m area. The results for RDX, HMX, TNT, and TNB are presented in Table 2.

RDX concentrations for the five discrete RDX values ranged from 0.78 to 24 mg/kg whereas concentration for the 5, 10, 20, and 40 multi-increment samples ranged from 6.0 to 14, 10 to 28, 7.1 to 14, and 6.5 to 13 mg/kg, respectively. This

reduction in the range of values as the number of increments increased was observed for the three other analytes as well. Subsequent sampling at hand grenade ranges utilized multi-increment samples with increments ranging from 20 to 100, and this approach resulted in a great improvement in reproducibility of replicate samples compared with characterization using discrete samples. At CFB-Petawawa, triplicate replicate 100-increment samples of the entire range resulted in mean concentrations of RDX, HMX, and TNT of 0.63 ± 0.25, 0.22 ± 0.07, and 0.14 ± 0.08 mg/kg, respectively. For purposes of estimating the mass of residues present at hand grenade ranges, these multi-increment sample estimates should be adequate in most cases.

Table 2. Concentrations of energetic residues for discrete and multi-increment surface soil samples at Fort Wainwright, Alaska, hand grenade range.

Sample type	N	Concentration range (mg/kg)			
		HMX	RDX	TNT	TNB
Discrete	5	0.38–3.5	0.78–24	0.02–3.7	0.02–0.41
5-increment	5	1.3–2.1	6.0–14	0.80–1.8	0.09–0.21
10-increment	5	2.0–4.5	11–28	0.68–2.7	0.14–0.29
20-increment	5	1.7–2.3	7.1–14	0.54–2.5	0.10–0.19
40-increment	5	1.5–2.1	6.5–13	0.35–1.9	0.09–0.18

A total of eleven active and two closed hand grenade ranges was sampled (Table 3). The old Castle range at CFB-Gagetown was active when it was first sampled in 1998 (Dube et al. 1999), but was inactive when sampled in 2002 and 2003 (Thiboutot et al. 2003). The target analytes detected at these ranges include RDX, TNT, HMX, TNB, 2ADNT, and 4ADNT. Of the analytes found, RDX usually is present at the highest concentration, with mean surface concentrations ranging from <0.01 to 51 mg/kg.

Table 3. Summary of results for energetic compounds detected in surface soils at hand grenade ranges.

Installation	Year sampled	Samples analyzed	Mean concentration (mg/kg)					
			HMX	RDX	TNT	TNB	4ADNT	2ADNT
Fort Lewis, WA[1,3]	2000	23*	1.8	7.5	9.3	0.05	0.15	0.13
	2001	5† (50)	1.0	4.4	1.5	ND**	ND	ND
Fort Richardson, AK[1,3]	2000	27*	0.02	0.08	0.03	ND	0.01	0.01
Camp Bonneville, WA[2]	2000	48*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fort Leonard Wood, MO[1]	2001	18† (30)	0.19	0.45	<0.01	<0.01	<0.01	<0.01
CFB-Shilo, Manitoba[1,4]	2001	15† (20)	0.05	0.71	0.06	<0.01	0.02	0.02
Fort Wainwright, AK[1]	2002	25† (1, 5, 10, 20, 40)	2	11	1.2	0.15	ND	ND
Schofield Barracks, HI[1]	2002	3† (30)	9.1	51	36	0.28	0.40	0.03
Pohakuloa Training Center, HI[1]	2002	7† (30)	0.53	5.6	0.78	<0.01	<0.01	<0.01
CFB Gagetown, New Brunswick	2002	5† (30)	0.02	0.12	0.12	<0.01	<0.01	<0.01
Old Castle Range[2,5]	2002	5† (30)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
New Castle Range[1,6] / New Castle Range[1,7]	2003	15† (25)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fort Polk, LA[1]	2003	2† (30)	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
CFB-Petawawa, Ontario[1]	2004	9† (25, 100)	0.18	0.65	0.16	<0.01	<0.01	<0.01

* Discrete samples

† Multi-increment samples with (n) increments per sample

** Not determined

[1] Active ranges

[2] Closed ranges

[3] Jenkins et al. 2001

[4] Ampleman et al. 2003b

[5] Dube et al. 1999

[6] Thiboutot et al. 2003

[7] Thiboutot et al. 2004

The hand grenade ranges appear to fall into two groups; one group of six ranges had concentrations of RDX less than 0.12 mg/kg and the other group of seven ranges had concentrations between 0.45 and 51 mg/kg (Table 3). Studies conducted by Hewitt et al. (2003) have estimated that about 25 µg of RDX and less than 1 µg of TNT are deposited on the soil surface when a hand grenade detonates as designed.

The relatively high concentrations of RDX, HMX, and TNT in the surface soils at Fort Lewis, Fort Wainwright, Schofield Barracks, and Pohakuloa (and probably those at Fort Leonard Wood, Canadian Force Base [CFB]-Shilo and CFB-Petawawa as well) cannot be explained by fragmentation grenades that detonated as designed. At all of these locations we found partially detonated carcasses of M67 (or C13) grenades (Fig. 2). In several instances, chunks of the high-explosive fill were observed next to these carcasses and the inside surfaces of these grenades were coated with high explosive. We are not certain whether these partial detonations occurred when the rounds were thrown or occurred when duds (grenades that did not detonate due to malfunction) were blown in place by explosives ordnance disposal (EOD) technicians using C4 explosive (91% RDX). In either case, we believe the high concentrations of residues observed at these seven ranges were due to these partial detonation events.

Once a partial detonation takes place, the multitude of normal high order detonations tends to disperse these residues across the range as usage continues. These partial detonations must be rare because about half of the ranges we studied had mean surface concentrations of less than 0.12 mg/kg; residue concentrations in this concentration range could have originated from the thousands of high-order detonations that occur annually at these ranges.

It is interesting that the mean concentration of RDX at the old Castle range at CFB-Gagetown was 5.6 mg/kg when it was sampled as an active range in 1998 (Dube et al. 1999), but the mean concentration was only 0.12 mg/kg after it had been closed and was resampled in 2002 (Thiboutot et al. 2003).

In most cases the highest concentrations of energetic compounds reside in the top few centimeters of soil. For example, at Fort Lewis where the surface is left undisturbed, 16 discrete sample pairs of surface soil and soil from a 10-cm depth were collected at locations ranging from 15 to 25 m from the throwing pit in July 2001 (Jenkins et al. 2001). The mean concentrations were 10.8 and 12.5 times greater in surface soils than at the 10-cm depth for RDX and HMX, respectively, and about 49 times greater for TNT in the surface relative to the 10-cm depth (Table 4). Depending on the management practices for a given range, however, residues can be deeper in the soil profile. For example at Fort Leonard Wood, the surface of the range is disked periodically and the concentrations of RDX, TNT,

and HMX were similar from the surface to a depth of 11 cm (Table 4). Soil samples were not collected at greater depths at these sites because of the fear of encountering live, undetonated hand grenades that had become buried by subsequent detonations.

a. Low-order hand grenade carcass.

b. Pieces from a low-order grenade.

Figure 2. Partially detonated grenade carcass and pieces from a low-order grenade found at Fort Lewis hand grenade range.

Table 4. Concentrations of energetic residues at various depths at the Fort Lewis and Fort Leonard Wood hand grenade ranges.

Soil depth (cm)	Mean concentration (mg/kg)					
	HMX	RDX	TNT	TNB	4ADNT	2ADNT
Fort Lewis, Washington						
0–1.5	1.8	7.5	9.3	0.05	0.15	0.13
10.0–12.5	0.14	0.69	0.19	0.02	0.06	0.08
Fort Leonard Wood, Missouri						
0–1.5	0.52	0.31	<0.01	0.02	<0.01	<0.01
1.5–3.0	0.83	0.81	<0.01	0.04	<0.01	<0.01
3.0–5.0	1.0	0.42	<0.01	0.03	<0.01	<0.01
5.0–7.0	0.54	0.57	<0.01	0.02	<0.01	<0.01
7.0–11.0	0.29	0.36	0.05	0.02	<0.01	<0.01

Antitank rocket range impact areas

Antitank rocket ranges are several hundred hectares in size and covered with low growing vegetation due to the necessity of maintaining a line-of-sight for training. Targets are usually derelict armored vehicles that are placed downrange at distances of 100 meters or more from the firing points. The weapon most often fired at these ranges is the 66-mm M72 light anti-armor weapon (LAW). This item (Fig. 3) contains M7 double-base propellant and the warhead contains 0.3 kg of the melt-cast explosive octol with either a tetryl or RDX booster, depending on the date of manufacture. M7 propellant for the LAW rocket contains 54.6% NC, 35.5% NG, 7.8% potassium perchlorate, 0.9% ethyl centralite, and 1.2% carbon black. Octol is composed of 70% HMX and 30% TNT.

At some ranges practice rounds are fired that contain propellant but do not contain octol. Field experiments were conducted at one closed and seven active antitank rocket ranges, including Fort Ord, California; CFB-Valcartier, Quebec; Yakima Training Center, Washington; Western Area Training Center (WATC)-Wainwright, Alberta; Fort Bliss, New Mexico; CFB-Gagetown, New Brunswick; Pohakuloa Training Center, Hawaii; and CFB-Petawawa, Ontario (Table 5).

The primary residue detected at antitank rocket range impact areas is HMX with concentrations in surface soils adjacent to targets generally in the hundreds of mg/kg (Table 5). TNT, RDX, 4ADNT, and 2ADNT are often detectable as well, but the concentrations are at least several orders of magnitude lower. HMX concentrations decline as the distance from the target increases (Fig. 4).

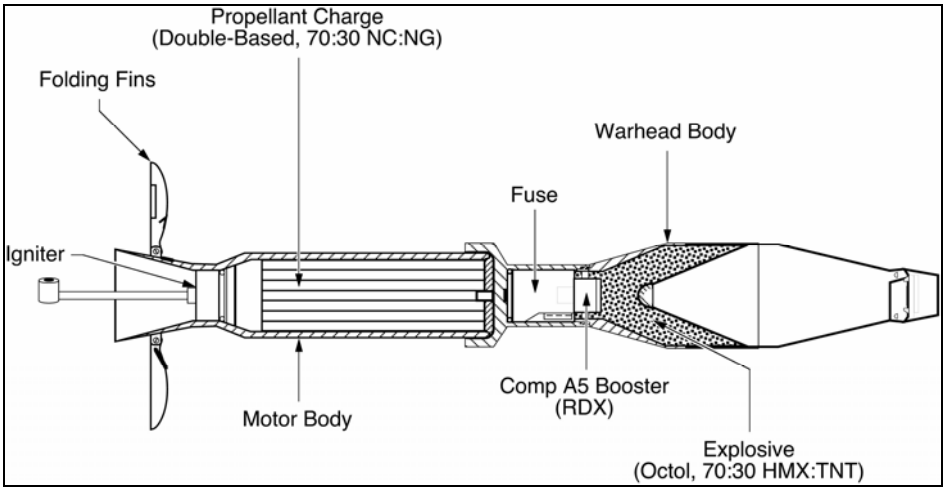


Figure 3. Diagram of 66-mm M72 LAW rocket.

Observations from site inspections indicate that LAW rockets frequently rupture upon impact without detonating, thereby depositing crystalline explosive over the soil surface. This deposition is thought to be the major source of explosives residues at the impact areas of these ranges. For example, soil samples were collected next to a ruptured M72 rocket at 0- to 0.5-cm, 2- to 6-cm, and 6- to 10-cm depths at Yakima Training Center, Washington. The concentration of HMX, TNT, and RDX declined from 10400, 358, and 46 mg/kg at the 0- to 0.5-cm depth, respectively, to 49, 1.7, and 1.5 mg/kg at 6- to 10-cm depth (Pennington et al. 2002).

Because the aqueous solubility of HMX is small (about 4–5 mg/L at 25°C), HMX tends to accumulate on the surface while the more soluble TNT (about 150 mg/L) dissolves, becomes associated with soil cation exchange sites, and undergoes environmental transformations (McCormick et al. 1976). The amino transformation products of TNT can covalently bind to soil organic matter, thereby becoming immobilized (Thorn et al. 2002). The HMX that slowly dissolves does not strongly interact with soils and can be carried through the vadose zone to underlying groundwater aquifers (Mailloux et al. 2000, in press). In most cases concern over the possible presence of buried unexploded ordnance has limited the collection of deep soil cores; however, soil samples were collected at the Fort Ord antitank rocket range to a depth of 120 cm (Fig. 5). In this case HMX was detectable at concentrations generally less than 1 mg/kg as deep as 120 cm whereas TNT, RDX, and amino transformation products of TNT were not detected at depths below 15 cm (Jenkins et al. 1998). Similar results were obtained for depth samples at other sites, although samples usually were not collected at depths below 15 cm.

Table 5. Concentrations of energetic compounds detected in surface soils adjacent to targets at antitank rocket ranges.

Installation[7]	Year sampled	Samples analyzed	Mean concentration (mg/kg)				
			HMX	RDX	TNT	4ADNT	2ADNT
CFB-Valcartier, Quebec[1,3,4]	1995	16*	803	4.6	24	<0.1	<0.1
	1995	5*	399	0.76	3	<0.1	<0.1
	1996	20*	662	<0.1	4	<0.1	<0.1
	2003	4† (30)	898	2.8	7	<0.1	<0.1
WATC-Wainwright, British Columbia[1,3]	1997	11*	987	5.3	126	<0.1	<0.1
Fort Ord, CA[2,5]	1997	8**	307	0.25	0.2	0.69	0.55
CFB-Gagetown, New Brunswick[1,4]	1998	10	680	<1	4	<0.1	<0.1
	2002	5†	874	0.5	6	0.8	0.7
	2003	8†	489	0.5	2	0.4	0.5
Yakima Training Center, WA[1,6]	2001	6† (30)	23	0.8	0.04	0.05	0.12
CFB-Petawawa, Ontario[1]	2004	3† (50)	745	0.32	73	<0.1	<0.1

* Composite samples

† Multi-increment samples with (n) increments per sample

** Discrete samples

[1] Active ranges

[2] Closed range

[3] Thiboutot et al. 1998

[4] Jenkins et al. 2004a

[5] Jenkins et al. 1998

[6] Pennington et al. 2002

[7] Impact areas at Pohakuloa and Fort Bliss anti-tank ranges were not sampled.

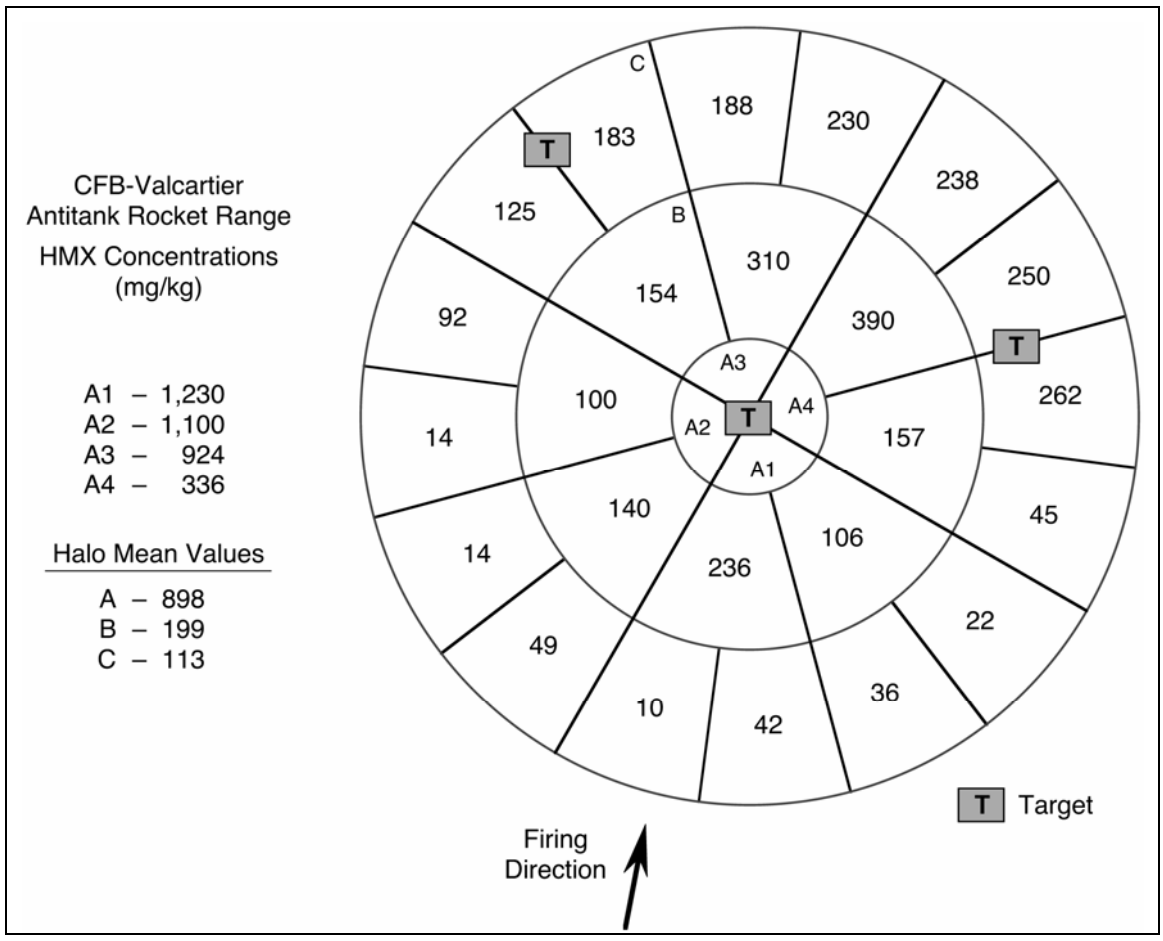
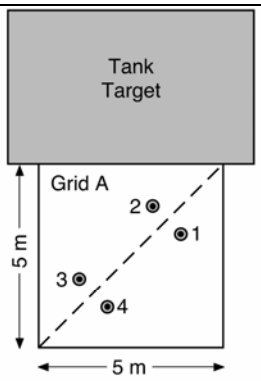


Figure 4. HMX concentrations at the target area of CFB-Valcartier antitank rocket range. (The position of the target is shown with a T.)

Because antitank rockets are propelled all the way to the target, propellants can still be present when these rockets detonate upon impact. Small pieces of propellant are thereby spread over the soil surface in the area around the targets. These residues can be seen visually and NG has been detected at the impact areas at concentrations as high as 23 mg/kg.

As with hand grenade ranges, collection of reproducible samples at antitank ranges has been problematic (Jenkins et al. 1999). At CFB-Valcartier, a 10-m × 10-m area just in front of a target was divided into one hundred 1-m × 1-m cells and a discrete sample was collected from the top 1.5 cm in each. The concentrations of HMX in these samples varied from 8 to 1520 mg/kg, demonstrating the futility in trying to represent the mean concentration for decision units using

discrete samples (Jenkins et al. 2004a, 2005). Multi-increment samples have been shown to provide more representative samples for characterizing the impact areas at these ranges (Jenkins et al. 2005). Here again, the use of machine grinding to reduce the soil particle size and an increase in sample size to 10 g were effective at minimizing the error due to compositional heterogeneity for samples collected at antitank range impact areas where HMX is the major contaminant (Walsh et al. 2002).



Sample 3

Sample Depth	Concentrations (mg/kg) HMX	RDX	TNT	4ADNT	2ADNT
0 – 15 cm:	479	0.2	0.2	0.4	0.2
15 – 30 cm:	4.3	< 0.1	< 0.1	< 0.1	< 0.1
30 – 45 cm:	1.3	< 0.1	< 0.1	< 0.1	< 0.1
45 – 60 cm:	0.2	< 0.1	< 0.1	< 0.1	< 0.1
105 –120 cm:	2.0	< 0.1	< 0.1	< 0.1	< 0.1

Sample 2

Sample Depth	Concentrations (mg/kg) HMX	RDX	TNT	4ADNT	2ADNT
0 – 15 cm:	302	0.6	0.1	1.2	1.0
15 – 30 cm:	1.0	0.1	< 0.1	< 0.1	< 0.1
30 – 45 cm:	0.4	< 0.1	< 0.1	< 0.1	< 0.1
45 – 60 cm:	0.2	< 0.1	< 0.1	< 0.1	< 0.1
105 –120 cm:	0.4	< 0.1	< 0.1	< 0.1	< 0.1

Sample 4

Sample Depth	Concentrations (mg/kg) HMX	RDX	TNT	4ADNT	2ADNT
0 – 15 cm:	136	0.1	0.1	0.7	0.6
15 – 30 cm:	0.6	< 0.1	< 0.1	< 0.1	< 0.1
30 – 45 cm:	0.4	< 0.1	< 0.1	< 0.1	< 0.1
45 – 60 cm:	0.3	< 0.1	< 0.1	< 0.1	< 0.1
105 –120 cm:	0.7	< 0.1	< 0.1	< 0.1	< 0.1

Sample 1

Sample Depth	Concentrations (mg/kg) HMX	RDX	TNT	4ADNT	2ADNT
0 – 15 cm:	273	0.5	0.1	1.1	0.9
15 – 30 cm:	0.7	< 0.1	< 0.1	< 0.1	< 0.1
30 – 45 cm:	0.7	< 0.1	< 0.1	< 0.1	< 0.1
45 – 60 cm:	0.7	< 0.1	< 0.1	< 0.1	< 0.1
105 –120 cm:	7.0	< 0.1	< 0.1	0.1	0.1

Figure 5. Concentrations of energetic compounds with depth at Fort Ord antitank rocket range impact area.

Table 6. Summary of results for nitroglycerin (NG) near firing points at active anti-tank rocket ranges.

Installation	Year sampled	Samples analyzed	Mean NG concentration (mg/kg)								
			In front					Behind			
			0–10 m	10–20 m	20–30 m	30–40 m	40–50 m	0–10 m	10–20 m	20–30 m	30–40 m
Yakima Training Center, WA[1]	2001	2 (30)*	3	NS**	NS	NS	NS	NS	NS	NS	NS
Schofield Barracks, HI[2]	2002	4 (30)*	NS	NS	NS	NS	NS	1200	9.4	NS	NS
CFB-Gagetown, New Brunswick[3,4]	2002	4 (30)*	176	65	NS	NS	14	1130	NS	NS	NS
	2003	15 (30)*	160	160	87	55	12	4700	2320	380	84
Fort Bliss, NM[5]	2002	10 (30)*	1	0.5	<0.1	NS	NS	1	NS	NS	NS
CFB-Valcartier, Quebec[6]	2003	13 (30)*	NS	4.2	0.8	0.1	0.4	910	490	104	NS
CFB-Petawawa, Ontario	2004	8 (40)*	NS	NS	NS	NS	NS	2240	380	NS	NS

* Multi-increment samples with (n) increments

** No sample collected

[1] Pennington et al. 2002

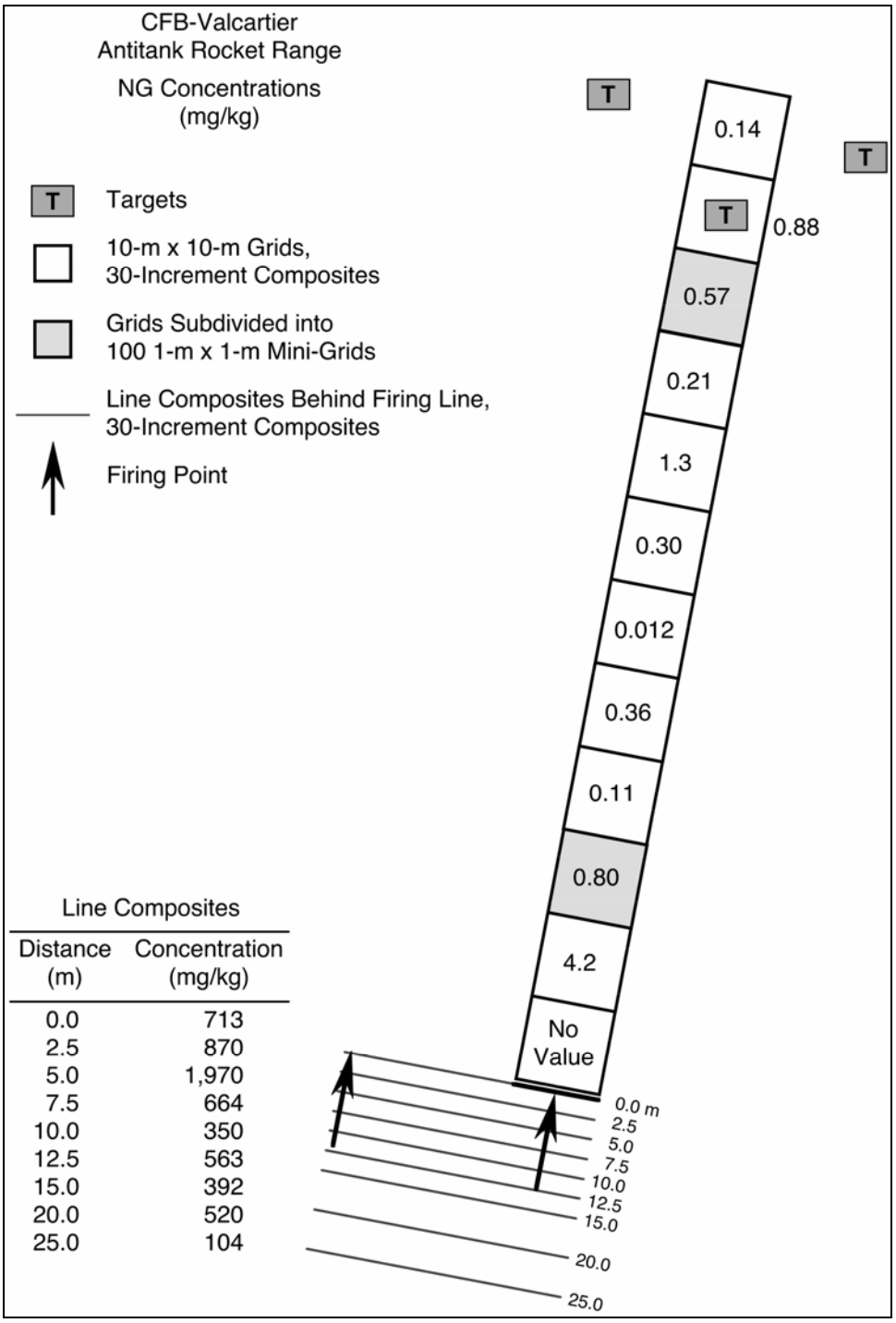
[2] Hewitt et al. 2004

[3] Thiboutot et al. 2003

[4] Thiboutot et al. 2004

[5] Pennington et al. 2003

[6] Jenkins et al. 2004a



Line Composites

Distance (m)	Concentration (mg/kg)
0.0	713
2.5	870
5.0	1,970
7.5	664
10.0	350
12.5	563
15.0	392
20.0	520
25.0	104

Figure 6. Concentrations of NG in multi-increment soil samples in front of and behind the rocket firing line at CFB-Valcartier antitank rocket range.

Antitank range firing points

Sampling has been conducted at six antitank rocket range firing points (Table 6). In all cases NG was the primary energetic compound detected, although only a few samples were analyzed for perchlorate. NG concentrations in surface soil samples from 0 to 25 m behind the firing line at CFB-Valcartier were generally in the hundreds of mg/kg, whereas concentrations between the firing line and the target were generally much lower (Fig. 6). Often a gravelly parking area is located behind the firing line at antitank rocket ranges and we sampled the soil at depths as great as 63 cm in this area at CFB-Gagetown in 2003 (Thiboutot et al. 2004). In one soil profile, NG concentrations declined from 20 mg/kg in the surface 0- to 5-cm depth to 6.4 mg/kg at the 20- to 27-cm depth, and to a concentration of about 0.2 mg/kg from the 40-cm depth to as deep as 60 cm (Table 7). Surface concentrations as high as 11,300 mg/kg were found at this site (Thiboutot et al. 2003).

At CFB-Valcartier we subdivided a 10-m × 10-m area 20–30 m in front of the firing line into one-hundred 1-m × 1-m cells and collected a discrete surface sample in each (0–2.5 cm). NG concentrations ranged from 0.02 to 3.4 mg/kg, indicating once again that discrete samples should not be used to estimate energetic concentrations for areas (decision units) near firing points (Jenkins et al. 2004a). A set of 50 30-increment samples was simulated using random numbers from this set of 100 discrete samples. The values obtained ranged from 0.34 to 0.93 mg/kg (Jenkins et al. 2004a). The value for the 30-increment sample actually collected within this 10-m × 10-m area was 0.80 mg/kg, well within the range simulated. Clearly the use of a 30-increment sample to estimate the mean concentration within this area provides a much more reproducible estimate than one or a small set of discrete samples.

Artillery ranges

Artillery ranges are the largest training ranges in the army inventory, covering an area of hundreds of square kilometers. Firing positions are often arranged around the circumference of the range with firing fans leading into the impact areas, generally positioned near the center of the range (Fig. 7). In the past, fixed firing points were established, but with more modern mobile artillery, firing activities have become more diffuse as training has evolved to support a “shoot and scoot” strategy. Once fired, artillery and mortar rounds travel several kilometers before impacting in the general vicinity of targets. The flight path takes these rounds over an area referred to as the firing safety fan, where only a very few defective rounds impact. Often, this is the largest area of the range. Once the rounds arrive near targets, most rounds are set to detonate upon impact.

Table 7. Nitroglycerin concentrations in depth profile samples collected in front of and behind the firing point at Wellington Antitank Range at CFB-Gagetown in 2003.

Location	Soil concentration (mg/kg)
Front, center of firing point, 10 m	**NG**
0–5 cm	11*
5–7 cm	15
7–11.5 cm	6.5
11.5–13 cm	0.06
13–18 cm	<d
18–22 cm	0.01
22–27 cm	<d
27–31 cm	0.02
31–35 cm	0.02
35–39 cm	0.01
39–42 cm	0.00
42–47 cm	0.00
47–52 cm	0.01
52–57 cm	0.01
Behind, center of firing point, 10 m	
0–5 cm	20
5–10 cm	14
10–20 cm	0.50
20–27 cm	6.4
27–35 cm	5.8
35–39 cm	0.32
39–42 cm	0.23
42–47 cm	0.15
47–50 cm	<d
50–56 cm	0.03
56–59 cm	0.22
59–63 cm	0.34

* Analysis by RP-HPLC (unshaded) and GC-ECD (shaded)

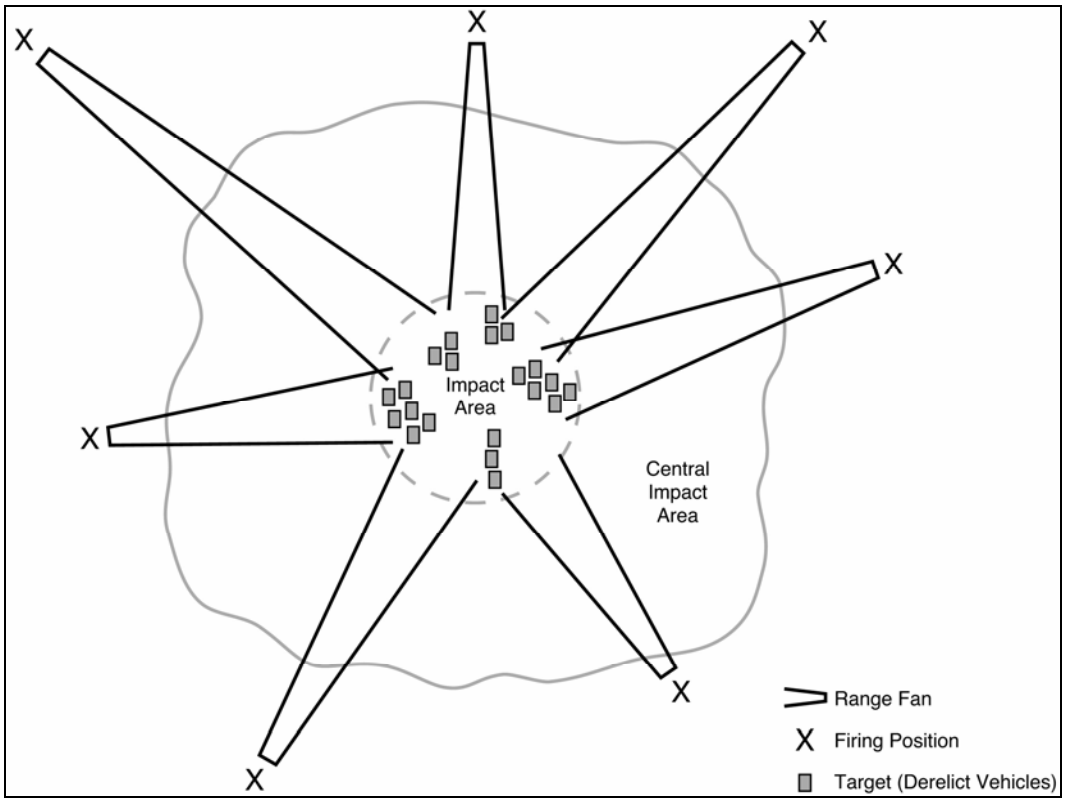


Figure 7. Schematic diagram of an artillery range showing firing points, range safety fan, and impact areas.

When the rounds perform as designed, these detonations result in the formation of a crater in the soil; the size is based on the type of round and the physical properties of the soil. Occasionally a round will impact without detonating, resulting in either a surface or subsurface UXO. For ranges where the soil is rocky or very hard, many of these UXO items can be seen on the surface. In a relatively small number of cases, a round will partially detonate upon impact, resulting in what is called a low-order detonation. In this case, only a portion of the explosive fill is consumed, sometimes leaving a substantial fraction of the explosive fill in or near the ruptured casing. Sometimes a high-order detonation will occur near enough to a surface UXO item that the item will be ruptured without detonation or with a low-order detonation. Here again, a substantial portion of the explosive fill will remain.

Climatic conditions and vegetative cover varies widely for the artillery ranges we have sampled in different parts of North America. For example, we have sampled ranges located in hot arid portions of the western United States (Pennington et al. 2003, Hewitt et al. 2005), ranges in subarctic Alaska and

Canada (Walsh et al. 2001, 2004; Ampleman et al. 2003a), a range located in a salt marsh in coastal Alaska (Walsh et al. 1995), ranges in moist southeastern United States (Jenkins et al. 2004b, Hewitt et al. 2005), ranges in a tropical setting in Hawaii (Hewitt et al. 2004), and ranges in cool, moist areas of eastern Canada (Thiboutot et al. 2003, 2004). Some ranges are sparsely vegetated, some heavily forested, some are open plains, and others are located in wetlands.

Many of the artillery ranges have been used for training for many decades. The munitions that have been fired include ordnance currently in the inventory as well as ordnance that was used pre- and post World War II, the Korean Conflict, and Vietnam. Because there has been no uniform management strategy in the past, UXO of a wide array of munitions are present on these ranges and many of these items are still live. For this reason access is tightly controlled and the length of time that we had access to the various ranges varied considerably.

The munitions fired to the greatest extent into these ranges are artillery and mortars, although various rockets, missiles, and Air Force and Navy bombs have been used as well. Currently the major munition systems being fired into these ranges include 155-mm howitzers, 105-mm howitzers, 120-mm main tank guns, 81-mm mortars, 60-mm mortars, and 120-mm mortars. Munitions including 90-mm recoilless rifle rounds, 4.2-in. mortar rounds, 8-in. artillery rounds, bombs of various sizes, 40-mm grenades, 106-mm high-explosive plastic (HEP) rounds, 2.75-in. LAW rockets, and TOW missiles also have been fired into some of these ranges. These munitions are delivered using single-, double-, triple-base gun propellants and rocket and missile propellants. Single-base propellant is composed of NC and 2,4-DNT, double-base propellant is composed of NC and NG, and triple-base propellant is composed of NC, NG, and nitroguanidine (NQ). The high explosives used in artillery and mortar warheads are generally either TNT or Composition B, although some older rounds also contained tetryl (methyl-2,4,6-trinitrophenyl nitramines). Some smoke-generating munitions contain white phosphorus (WP). Bombs that have been dropped in some of these ranges contain TNT or tritonal (TNT and aluminum), 40-mm grenades contain Composition A5 (RDX), and LAW rockets contain octol (HMX and TNT).

A listing of the 16 artillery ranges where we have collected samples is shown in Table 8. After each installation, we have indicated the types of areas sampled. Because at the beginning of this work there was very little information about energetic residues on these ranges, we sampled a variety of areas, including firing points, target areas, areas in and near detonation craters, areas adjacent to UXO items, areas where chunks of explosive were observed on the surface, areas where a round had undergone a low-order detonation, and areas that were away from the firing points or targets but were within the firing safety fans.

Table 8. Installations at which artillery ranges have been sampled for energetic residues.

Installation	Year sampled	Types of areas sampled						
		Firing points	Target areas	Areas with partial detonations	Firing fan areas*	Craters	Near-UXO items	Areas with chunk explosives
Fort Richardson, AK[1]	1992	x	x					
Fort Greely (Donnelly Training Area), AK[2]	2000	x						
Fort Lewis, WA[3]	2000	x	x			x		
Yakima Training Area, WA[3]	2001	x	x			x	x	
Camp Guernsey, WY[3]	2001		x	x				x
CFB-Shilo, Manitoba[4]	2001		x		x			
Fort Bliss, NM[5]	2002	x	x	x	x			x
Jefferson Proving Ground, IN	2002		x		x			
Schofield Barracks, HI[6]	2002	x	x		x			
CFB-Gagetown, New Brunswick[7, 8]	2002 2003		x	x	x			x
Fort Polk, LA[9]	2003		x	x	x			x
Fort Hood, TX[10]	2004		x	x			x	x
Fort Carson, CO[10]	2004	x	x					
29 Palms, CA[10]	2004		x	x				x
Massachusetts Military Reservation, MA	2004		x					
CFB-Petawawa, Ontario	2004	x						

* Areas away from any known firing activity or detonations

1 Walsh et al. 1995
2 Walsh et al. 2001
3 Jenkins et al. 2001
4 Thiboutot et al. 2003
5 Pennington et al. 2003
6 Hewitt et al. 2004
7 Ampleman et al. 2003b
8 Thiboutot et al. 2004
9 Jenkins et al. 2004b
10 Hewitt et al. 2005

Table 9. Summary of sampling results for surface soils at artillery firing points.					
			Mean surface soil concentration (mg/kg)		
Installation	**Weapon fired**	**Propellant type**	**2,4-DNT**	**2,6-DNT**	**NG**
Fort Greely (Donnely Training Area), AK	105-mm howitzer	single base			
FP BoWhale			4.3	NA	<0.01
FP Big Lake			9.1	0.35	<0.01
FP Mark			1.1	NA	NA
FP Sally			0.66	NA	NA
Yakima Training Center, WA	120-mm tank gun	single, triple base			
MPRC: 10 m from fixed firing point			24	0.40	4.6
MPRC: 20 m from fixed firing point			8.2	0.13	1.3
MPRC: 30 m from fixed firing point			2.2	<0.01	0.64
MPRC: 50 m from fixed firing point			0.68	<0.01	0.33
MPRC: 75 m from fixed firing point			0.19	<0.01	0.50
Yakima Training Center, WA	155-mm howitzer	single, triple base			
7 m from firing point			<0.03	<0.02	26
12 m from firing point			<0.03	<0.02	3.0
22 m from firing point			3.2	0.05	6
32 m from firing point			0.27	<0.02	1.85
Fort Bliss, NM (14 composite samples)	155-mm howitzer	single, triple base			
Non detects: 12 samples			<0.002	<0.001	<0.001
Maximum value found			0.97	<0.001	<0.001

Table 9 (cont'd).

Installation	Weapon fired	Propellant type	Mean surface soil concentration (mg/kg)		
			2,4-DNT	2,6-DNT	NG
Fort Lewis, WA (600 rounds fired)*					
At muzzle of 105-mm howitzer	105-mm howitzer	single base	63	<0.01	<0.01
5 m from muzzle			84	<0.01	<0.01
10 m from muzzle			57	<0.01	<0.01
15 m from muzzle			15	<0.01	<0.01
20 m from muzzle			4.0	<0.01	<0.01
CFB-Petawawa, Ontario	various mortars	single, double base	0.91	<0.01	3.58
Schofield Barracks, HI					
Max in seven composite samples	105-mm and 155-mm	single, triple base	0.04	<0.01	0.35
Fort Richardson, AK					
surface 0- to 3-cm depth	105-mm howitzer	single base	9.6	<0.01	<0.01
3- to 6-cm depth†			2.2	<0.01	<0.01
6- to 10-cm depth†			0.063	<0.01	<0.01
10- to 20-cm depth†			0.56	<0.01	<0.01
Fort Carson, CO	Mostly mortars	mostly double base	0.11	<0.01	12

* Surface samples collected from top 0.5 cm of surface soil

† Soils collected at specified depths below surface

Artillery range firing points

A number of firing point areas have been sampled at various artillery ranges (Table 8). These have included areas where 105-mm and 155-mm howitzers have been fired, an area where various mortars were fired, and an area where 120-mm tank guns were fired (Table 9). The largest amount of sampling was conducted in areas where 105-mm howitzers were fired. The propellant used for these guns is single base and 2,4-DNT was found to be the residue present at the highest concentration in all cases. We did not attempt to determine the concentration of NC because it is polymeric and does not present a problem for off-site migration, which is the major concern for energetic residues. Also, there are no validated methods for this compound when dispersed in a soil matrix.

The highest concentrations of 2,4-DNT are for samples from Fort Lewis (Jenkins et al. 2001), but these were collected from an area just in front of 105-mm howitzers where 600 rounds had been fired in the preceding month, and the samples were collected from only the top 0.5 cm of soil. When the concentration of 2,4-DNT in a sample was above 3 mg/kg, we sometimes detected much lower concentrations of 2,6-DNT as well. 2,6-DNT is an impurity in military-grade 2,4-DNT. Soil samples were collected primarily in surface soils, except at Fort Richardson, where soils were sampled as deep as 20 cm. In this case the concentration of 2,4-DNT declined from 9.6 mg/kg in the surface 0- to 3-cm sample to 0.56 mg/kg in the sample from 10 to 20 cm. To investigate the physical nature of these propellant residues, metal trays were placed in front of 105-mm howitzers during a firing event at Fort Richardson, Alaska. Microscopic analysis of the residues indicated that at least a portion of the residues was unburned or partially burned propellant fibers with fiber lengths ranging from 0.4 to 7.5 mm (Taylor 2004 and personal communication[*]). The unburned fibers contained much higher concentrations of 2,4-DNT than did the partially burned ones.

At Yakima Training Center we were able to collect surface soil samples at a multi-purpose range complex in front of a fixed firing point for 120-mm tank firing (Pennington et al. 2002). Both 2,4-DNT and NG were detected at 75 m, the farthest distance from the firing point sampled (Table 9). At Yakima we also sampled an area where a 155-mm howitzer had recently been fired. In this case, the residue was largely NG although some 2,4-DNT was also detected. The propellants used with 155-mm howitzers can be either single base for short range target practice or a combination of single base and triple base for longer range firing activities.

[*] Personal communication, Susan Taylor, CRREL, 2004.

Samples from areas at artillery ranges away from impact areas and firing points

At Camp Shelby, Mississippi; Fort Bliss, New Mexico; Fort Polk, Louisiana; Fort Carson, Colorado; and Jefferson Proving Ground, Indiana, the U.S. Army Environmental Center (USAEC) and the U.S. Army Center for Health Promotion and Preventive Medicine (CHPPM) conducted Regional Range Studies to assess the overall environmental impacts of residues from firing activities on artillery ranges. The USAEC/CHPPM group used a stratified random sampling strategy unbiased by any judgmental observations, and collected 5-point composite samples from 10-m × 10-m grids established at various points across these areas. Because target areas represent only a small fraction of the total area of artillery ranges and their sampling area selection was unbiased, most of the areas that they sampled were quite a distance from any recognizable activity. We accompanied the USAEC/CHPPM sampling teams at all of these sites with the exception of Camp Shelby, and we collected random 30-increment samples within some of the same 10-m × 10- m grids that they sampled. Most of these samples collected by both the USAEC/CHPPM and CRREL protocols for these sampling locations did not contain detectable energetic residues using either RP-HPLC or GC-ECD methods, indicating that most of the total area at these ranges is virtually uncontaminated (Table 10).

At CFB-Shilo, Manitoba, and CFB-Gagetown, New Brunswick, Thiboutot et al. (2003, 2004) collected sets of multi-increment samples at various distances between the firing points and targets. Here again, the concentrations of energetic compounds were generally near or below analytical detection limits (Table 10), indicating that the largest portion of the range has very low concentrations of energetic residues. We also collected a set of 77 50-increment samples and a set of 16 discrete samples using a grid node sampling approach from the Washington Range at Fort Greely. This range is used to test artillery, mortar, TOW missiles, and a variety of other weapons under very low temperature conditions and has been used for many years. Of the 77 multi-increment samples, 74 had no detectable residues of energetic compounds, and the maximum concentrations for the other three samples were 0.61 mg/kg for HMX, 0.62 mg/kg for 2,4-DNT, and 0.27 mg/kg for RDX. Of the 16 discrete samples, 10 had no detectable residues and the maximum concentrations for RDX, TNT, HMX, 2,4-DNT, 2,6-DNT, 4ADNT, and 2ADNT were 0.036, 0.012, 0.004, 9.5, <0.03, 0.016, and 0.018 mg/kg, respectively (Walsh et al. 2001). Similar sets of 50-increment samples were collected on the west side of the Washington range and at the Georgia Island range using the grid-node approach. No energetic residues were detected in any of the 68 samples analyzed.

Table 10. Results for unbiased samples collected at artillery range areas that were within the firing fan but away from firing points and targets.

Installation	Number of samples analyzed	Number of samples with no detectable energetic compounds		Maximum concentration (mg/kg)						
				RDX	TNT	HMX	2,4-DNT	NG	4ADNT	2ADNT
Camp Shelby, MS (AEC/CHPPM)[1]	54	53		<0.23	<0.23	0.33	<0.23	<0.48	<0.23	<0.23
Fort Bliss, NM (AEC/CHPPM)[2]	161	151		8	0.20	2.7	<0.001	0.35	0.27	0.19
Fort Bliss, NM (ERDC)[3]	23	14		0.009	0.049	0.066	0.011	0.97	0.011	0.012
Jefferson Proving Ground, IN (AEC/CHPPM)[4]	170	138/RDX 167/TNT 169/DNT		0.098	0.06	<0.05	0.58	<0.05	<0.05	<0.02
Jefferson Proving Ground, IN (ERDC)	105	103/RDX 100/TNT		0.036	0.232	<0.05	<0.001	<0.05	<0.001	<0.001
Fort Polk, LA (AEC/CHPPM)[5]										
CFB-Shilo, MN (DRDC/ERDC)[6]	26	16		0.022	1.6	<0.01	0.046	0.015	<0.001	<0.001
CFB-Gagetown, New Brunswick (DRDC/ERDC)[7]	18	7		<0.05	0.21	<0.05	0.02	0.49	<0.01	<0.01
Fort Greely (Donnelly Training Area), AK (ERDC)										
WA Range: 50-increment samples	77	74		0.27	<0.001	0.61	0.62	<0.02	<0.002	<0.002
WA Range: discrete samples[8]	16	10		0.036	0.012	0.004	9.5	<0.03	0.016	0.018
Georgia Island Range: 50-increment samples[9]	44	44		<0.002	<0.001	<0.004	<0.001	<0.02	<0.002	<0.002
West side of WA Range: 50-increment samples[9]	24	24		<0.002	<0.001	<0.004	<0.001	<0.02	<0.002	<0.002
Total	718	631	Maximum	8	1.6	2.7	9.5	0.97	0.27	0.19

[1] USACHPPM 2001
[2] USACHPPM 2004
[3] Pennington et al. 2003
[4] USACHPPM 2003
[5] USACHPPM 2005
[6] Ampleman et al. 2003b
[7] Thiboutot et al. 2003
[8] Walsh et al. 2001
[9] Walsh et al. 2004

Table 11. Analytical results for individual soil samples collected near artillery targets.								
Installation	# of increments per sample	Distance from target (m)	Mean concentration (mg/kg)					
			HMX	RDX	TNT	4ADNT	2ADNT	TNB
Camp Guernsey, WY[1]	30	1	0.14	<0.03	<0.02	<0.03	<0.04	<0.02
	30	5	<0.03	0.003	0.003	0.02	0.01	<0.003
	30	10	<0.03	<0.003	0.013	0.04	0.03	<0.003
	30	15	<0.03	<0.003	<0.001	0.01	0.007	<0.003
Fort Bliss, NM: (Target 1)[2]	30	2	3.1	2.1	0.69	0.1	<0.01	<0.01
Fort Bliss, NM: (Target 1)	30	5	0.03	0.01	0.57	0.08	<0.01	<0.01
Fort Bliss, NM: (Target 2)	30	2	<0.03	<0.003	<0.001	<0.002	<0.01	<0.01
Fort Bliss, NM: (Target 3)	30	2	<0.03	<0.003	<0.001	0.04	<0.01	<0.01
Fort Bliss, NM: (Target 4)	30	2	0.02	0.01	0.02	0.02	<0.01	<0.01
Fort Bliss, NM: (Target 5)	30	2	0.08	0.37	<0.01	0.002	<0.01	<0.01
Fort Bliss, NM: (Target 5)	30	5	0.04	0.03	<0.001	<0.01	<0.01	<0.01
Fort Hood, TX[3]	10	0–2	0.010	0.016	0.006	<0.01	<0.01	<0.01
	10	0–2	<0.01	0.003	<0.01	<0.01	<0.01	<0.01
	10	0–2	<0.01	0.013	0.008	0.004	0.007	<0.01
	10	2–5	<0.01	0.008	<0.01	<0.01	<0.01	<0.01
	10	2–5	<0.01	<0.01	0.021	0.004	0.004	<0.01
	10	2–5	<0.01	0.010	0.059	0.040	0.040	<0.01
	10	2–5	<0.01	0.007	0.007	0.004	0.007	<0.01
	10	5–10	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	10	5–10	<0.01	<0.01	0.013	<0.01	<0.01	<0.01
	10	10–20	0.092	0.14	<0.01	<0.01	<0.01	<0.01
	10	10–20	0.011	0.037	<0.01	0.009	0.009	<0.01
	10	10–20	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	10	10–20	<0.01	<0.01	0.005	0.007	0.007	<0.01

Table 11 (cont'd). Analytical results for individual soil samples collected near artillery targets.								
Installation	# of increments per sample	Distance from target (m)	Mean concentration (mg/kg)					
			HMX	RDX	TNT	4ADNT	2ADNT	TNB
Fort Polk, LA[4]	10	0–2	15	16	1.2	0.25	0.31	<0.01
	10	0–2	1.40	1.20	0.14	0.17	0.21	<0.01
	10	0–2	0.42	2.2	0.52	0.28	0.36	<0.01
	10	2–5	0.36	0.50	19	0.91	1.20	0.082
	10	2–5	0.88	0.45	0.44	0.17	0.23	<0.01
	10	2–5	0.24	0.72	0.076	0.074	0.096	<0.01
	10	2–5	0.22	1.8	14	0.27	0.25	<0.01
	10	2–5	0.12	0.42	0.23	0.18	0.27	<0.01
	10	2–5	1.9	13	4.4	0.53	0.73	<0.01
	10	2–5	0.23	1.2	2.2	0.61	0.88	<0.01
	10	2–5	0.13	0.29	9.5	1.1	1.4	<0.01
	10	2–5	0.064	0.11	0.78	0.30	0.40	<0.01
Fort Greely, AK[5,6]	7	5	<0.01	0.002	<0.001	<0.001	<0.001	<0.001
	7	5	<0.01	0.004	<0.001	<0.001	<0.001	<0.001
	7	10	0.11	0.002	0.002	<0.001	<0.001	<0.001
	7	10	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001
	7	15	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001
	7	15	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001
	7	20	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001
	7	20	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001
	7	25	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001
	7	25	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001
	7	30	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001
	7	30	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001

Table 11 (cont'd).

Installation	# of increments per sample	Distance from target (m)	Mean concentration (mg/kg)					
			HMX	RDX	TNT	4ADNT	2ADNT	TNB
Fort Greely, AK[5, 6] (cont'd)	7	35	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001
	7	35	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001
	7	40	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001
	7	40	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001
	7	45	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001
	7	45	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001
	7	50	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001
	7	50	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001

[1] Pennington et al. 2002
[2] Pennington et al. 2003
[3] Hewitt et al. 2005
[4] Jenkins et al. 2004b
[5] Walsh et al. 2001
[6] Wire-guided missile target

Artillery range target areas

Because target areas receive the largest numbers of detonations per unit area, we collected samples systematically around targets at many of the artillery ranges that we visited. These targets are generally derelict trucks, tanks, and armored personnel carriers, and many have sustained enormous damage after years of target practice. Because of the danger of encountering buried UXO items and the fact that most detonations scatter residue over the surface, most of the soil samples from these areas were collected from surface soil.

Table 11 presents a series of results from the analysis of surface soils collected near targets at five artillery impact areas. At Camp Guernsey, Wyoming, we collected a series of duplicate 30-increment samples at distances of 1, 5, 10, and 15-m from the perimeter of a truck target. HMX, RDX, TNT, 4ADNT, 2ADNT, and TNB were detected in at least one of these samples, but except for one HMX value at 0.14 mg/kg, concentrations were less than 0.05 mg/kg. At Fort Bliss, New Mexico, we collected 30-increment samples at distances of 2 and 5 meters from the target perimeter. Concentrations of HMX, RDX, TNT, 4ADNT, 2ADNT, and TNB were always less than 1 mg/kg, except for one 2-m sample at Target Number 1 where HMX and RDX were 3.1 and 2.1 mg/kg, respectively. At Fort Hood, 10-increment samples were collected at distance intervals of 0–2 m, 2–5 m, 5–10 m, and 10–20 m. Concentrations for the same six analytes were always less than 0.14 mg/kg. Soil samples collected from 0–2 and 2–5 m around a target area at Fort Polk had the highest concentrations of these target analytes, with maximum values for HMX, RDX, TNT, 4ADNT, 2ADNT, and TNB of 15, 16, 19, 1.1, 1.4, and 0.082 mg/kg, respectively. At Fort Greely, Alaska, we collected 20 seven-increment samples at distances ranging from 5 to 50 m from a target used for testing TOW missiles. In only three of these samples were energetic compounds detected and the maximum concentration was 0.11 mg/kg for HMX.

We also collected a set of six systematic 100-increment samples in a 100-m × 100-m area next to a target at Fort Hood, Texas. This area had over 600 craters within the 10,000-m^2 area, 55 of which were considered to be recent (within the last several months). The mean and range (r) of values obtained for these six samples were RDX (mean = 1.2 mg/kg, r = 0.12 to 3.68 mg/kg), TNT (mean = 0.30 mg/kg, r = <0.001 to 0.81 mg/kg), and HMX (mean = 0.21 mg/kg, r = 0.035 to 0.63 mg/kg). A set of 36 discrete samples was also collected within this area. RDX was detected in only seven of these samples, HMX was detected in eight, and TNT was not detected in any. However, the TNT transformation products (4ADNT and 2ADNT) were detected in two of these samples. It should be noted, though, that a small area that had visible chunks of Composition B was found

within this 10,000-m^2 area, and this may account for the low levels of residues detected in the multi-increment samples, and the low frequency of detections in the set of discrete samples.

Overall, the concentrations of energetic compounds near artillery targets are low and there does not appear to be a defined concentration gradient. Surface soil samples from some targets can have concentrations in excess of one mg/kg, but the concentrations at most targets are less, sometimes below the detections limits of the analytical methods used. In many cases we used SW846 Method 8095 (EPA 1999) for samples from artillery range impact areas because the concentrations of energetic compounds were less than the detection limits of the RP-HPLC method, SW846 Method 8330 (EPA 1994).

Artillery ranges near low-order (partial) detonations

By far the highest concentrations of energetic residues that we encountered at artillery ranges were associated with rounds that had undergone a low-order detonation (Table 12). One example of these partial detonations is shown in Figure 8. In most cases chunks of pure explosive were observed on the soil surface near these items and concentrations of energetic compounds in the surface soil (particles <2 mm) were at the percent levels in a few cases (Table 12). The highest concentration that we encountered for a soil sample was from Fort Hood where the TNT concentration beneath a low-order 4.2-in. mortar was 143,000 mg/kg (14.3%). The areas influenced by these low-order detonations were explored in several cases. At Fort Polk we collected a set of 100 discrete samples in a 10-m × 10-m area that was subdivided into 100 1-m × 1-m cells (Jenkins et al. 2004b). The visible mass of Composition B on the surface of each cell was collected and weighed separately from the soil samples. The RDX concentrations in these soil samples varied from 0.037 to 2390 mg/kg (Fig. 9) and the highest concentrations, i.e., those >100 mg/kg, were isolated in two small areas near where chunks of pure explosive were observed on the surface. About two-thirds of the total RDX present within this area was in the soil-sized fraction (<2 mm) and only about one-third in the visible chunks found on the surface. Some of the locations of these low-order detonations were near targets, but many others were found as we traversed the range in areas away from any recognizable targets. We believe that these low-order detonations and UXO items that have been ruptured by subsequent detonations represent the main source of residues on artillery ranges.

Table 12. Concentration of energetic compounds in surface soil samples near low-order detonations at artillery ranges.

Installation	Description of surface soil samples	Concentration (mg/kg)						
		HMX	RDX	TNT	4ADNT	2ADNT	TNB	2,4-DNT
Fort Greely, AK[1]	Beneath a low-order 2.75-in. rocket warhead	40	340	130	1	0.8	0.2	0.04
Fort Lewis, WA[2]	Beneath a low-order 155-mm round	<10	<10	15,100	110	102	15	40
Camp Guernsey, WY[3]	Beneath a ruptured 500-lb bomb	<10	<10	9,440	<10	<10	50	<10
Yakima Training Center, WA[3]	Near a low-order 155-mm round	5.2	54	<1	<1	<1	<1	<1
Fort Bliss, NM[4]	Beneath a low-order 2.75-in. rocket warhead	302	1,130	14	3.3	2.8	<1	<1
Fort Bliss, NM[4]	Beneath a low-order 155-mm round	<10	<10	2,520	<10	<10	148	<10
Fort Bliss, NM[4]	Beneath a 90-mm round	149	678	1,110	12	18	9	1.3
29 Palms, CA[5]	Beneath a chunk of Composition B from low-order 155-mm	94	825	537	0.05	0.11	4	<0.1
CFB-Gagetown, NB[6]	Within a crater from a low-order 500-lb bomb	<10	<10	42,200	<10	<10	<10	<10
Fort Carson, CO[5]	Beneath a low-order 106-mm HEP round	59	<1	336	<1	<1	<1	<1
Fort Carson, CO[5]	Beneath ruptured 8-in. round	53	308	451	6	5	0.3	1
Fort Hood, TX[5]	Beneath a low-order 4.2-in. mortar	59	323	143,000	<10	20	26	26

[1] Walsh et al. 2001
[2] Jenkins et al. 2001
[3] Pennington et al. 2002
[4] Pennington et al. 2003
[5] Hewitt et al. 2005
[6] Thiboutot et al. 2003

Figure 8. Low-order 155-mm artillery round found at Fort Bliss.

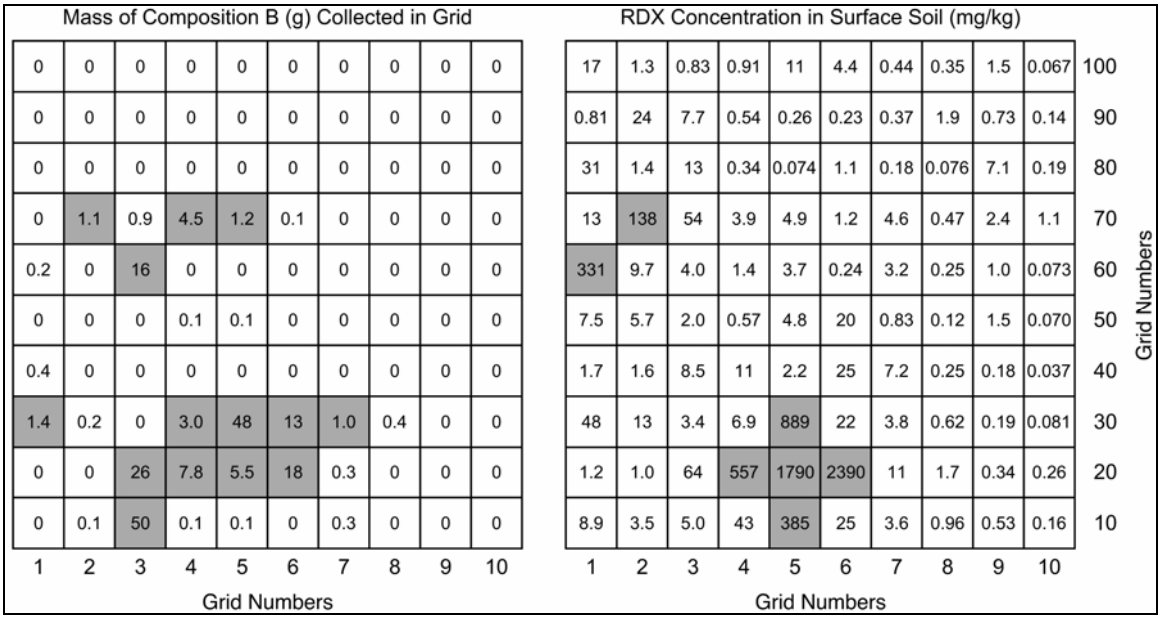


Figure 9. Mass of Composition B and soil RDX concentrations and their relative position in the 10-m × 10-m sampling grid near a low-order 81-mm mortar round at Fort Polk's artillery range impact area.

Bombing ranges

Air Force ranges are very large, generally hundreds of square kilometers in size, but the areas currently used for training with high-explosives-containing bombs are much smaller, generally only tens of hectares. We sampled two live-fire bombing ranges: Cold Lake Air Weapons Range (CLAWR) in Alberta (Ampleman et al. 2003a, 2004) and Holloman Air Force Range (HAFB) in New Mexico (Jenkins et al. in press). We also sampled several other ranges where bombing with HE-containing bombs had been conducted (Donnelly Training Area, Alaska; Camp Guernsey, Wyoming; Fort Polk, Louisiana; CFB-Gagetown, New Brunswick; 29 Palms, California; and Fort Carson, Colorado). The Air Force conducts regularly scheduled range maintenance activities where duds and chunks of high explosive (larger than golf-ball size) observed on the surface are gathered up and destroyed by detonating with C4, and craters are often filled in.

The high explosive present in U.S. and Canadian Air Force bombs is usually either tritonal (TNT, aluminum powder) or H-6 (TNT, RDX, aluminum powder). Some older bombs contained TNT. Although experiments documenting the residue deposited when a bomb detonates as designed have not been conducted, experimental results for large artillery rounds indicate that large mass HE

detonations are very efficient, dispersing only microgram-to-milligram quantities of residue when they detonate high order (M.R. Walsh et al. 2005). As with other ordnance items, low-order detonations are the major source of residues from bombs.

Figure 10. Reddish-colored crater formed from a low-order 500-lb bomb at CFB-Gagetown.

Figure 10 shows a low-order bomb crater at CFB-Gagetown where the TNT dissolving from chunks of tritonal in the bottom of the crater turned red as a result of photodegradation. Communication with range personnel at CLAWR indicates that low-order bomb detonations generally occur several times per year at their range. A low-order bomb can deposit kilogram quantities of residues as chunks and soil size particles. We observed low-order bombs at Camp Guernsey (Fig. 11) and at HAFB.

Figure 11. Low-order bomb found on the impact range at Camp Guernsey, Wyoming.

Because of the very large amount of explosive that remains after a low-order detonation, we believe it is these occurrences that produce the largest mass of residue at bombing ranges. Some of these low-order events probably occur during the bombing exercise, but the one we observed at HAFB was apparently caused by a bomb detonation occurring in close proximity to a subsurface 2000-lb dud (Fig. 12). Bomb detonations produce many sharp metal fragments, as designed, and these high-velocity fragments can rupture UXOs present nearby. This phenomena is believed to happen on a frequent basis on training ranges where intense live-fire training is conducted in areas where many UXO have accumulated over the years. This has been simulated in a PhD study (Lewis 2004) where munitions were easily broken by fragments from detonations of other rounds nearby and the fate of explosive from broken shells was measured in soil columns (Pennington et al. 2004).

Figure 12. Soil sampling being conducted near a low-order 2000-lb bomb at Holloman Air Force Base, New Mexico.

Results for soil samples collected at CLAWR, HAFB, near a low-order bomb at Camp Guernsey, at the bombing areas at Fort Polk, and near some low-order bomb craters at CFB-Gagetown are presented in Table 13. The concentration of TNT in these samples from the single bombing target at CLAWR ranged from 3 to 408 mg/kg, with a mean value of 86 mg/kg for a 50-m-radius circle. The mean concentrations of RDX, HMX, 4ADNT, 2ADNT, 2,4-DNT, and TNB in these samples were 0.27, 0.21, 0.71, 1.2, 0.20, and 0.13 mg/kg, respectively. Because the TNT concentrations were two orders of magnitude higher than RDX, and we observed several small chunks of tritonal present in the sampled area, we believe that these residues were from a tritonal-containing bomb. Because the soil around the target at CLAWR is tilled to reduce the chance of a wild fire, residue concentrations for different samples are less heterogeneous than those encountered at some other ranges.

Table 13. Concentrations of energetic residues at live-fire bombing range impact areas.								
		Concentration (mg/kg)						
Installation	**Distance from target**	**TNT**	**RDX**	**HMX**	**4ADNT**	**2ADNT**	**2,4-DNT**	**TNB**
Cold Lake Air Weapons Range, AB 2003a	0–10 m (mean n = 2)	32.2	<0.01	<0.01	1.14	1.78	0.17	0.08
	10–30 m (mean n = 8)	83.3	0.56	0.14	0.91	1.39	0.20	0.06
	30–50 m (mean n = 16)	94.1	0.1	0.23	0.62	1.04	0.1	0.17
Cold Lake Air Weapons Range, AB 2004	0–10 m (mean n = 2)	41.1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	10–30 m (mean n = 8)	44.4	0.05	<0.01	0.12	0.19	<0.01	<0.01
	30–50 m (mean n = 16)	41.6	0.38	0.10	<0.01	<0.01	<0.01	<0.01
Holloman AFB, NM (d)	**Area sampled**							
	within low-order bomb crater	60.0	<0.1	<0.1	0.19	0.19	0.20	0.69
	100 m x 100 m*	5.94	0.09	0.03	0.10	0.12	0.03	0.02
	100 m x 100 m†	0.58	0.01	<0.01	0.01	0.07	<0.01	0.04
	10 m x 10 m*	16.1	<0.01	<0.01	0.60	0.61	0.09	0.051
	10 m x 10 m†	0.28	<0.01	<0.01	0.01	0.02	<0.01	<0.01
Camp Guernsey, WY (c)	**Low-order bomb**							
	3 m from bomb	13.0	0.09	0.03	1.86	1.44	0.03	0.16
	5 m from bomb	0.26	<0.03	<0.03	0.30	0.23	<0.03	<0.01
	10 m from bomb	0.30	<0.03	<0.03	0.06	0.04	<0.03	<0.01
Fort Polk, LA	**Area near large bombing craters**							
	inside/toe crater #1	0.01	<0.01	<0.01	0.02	0.02	<0.01	<0.01
	rim crater #1	<0.01	<0.01	<0.01	0.02	0.02	<0.01	<0.01
	bottom crater #2	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	toe to rim crater #2	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	sides crater #2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	sides crater #2	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Table 13 (cont'd).

Installation	Distance from Target	Concentration (mg/kg)						
		TNT	RDX	HMX	4ADNT	2ADNT	2,4-DNT	TNB
CFB-Gagetown, NB	**Low-order bomb crater**							
	Crater #2 at 1 m	276	0.08	0.25	2.8	4.5	0.57	0.59
	crater #2 at 2 m	334	<0.01	<0.10	1.2	1.8	0.20	0.45
	Crater #3 at 1 m	17.6	<0.01	<0.10	<0.10	<0.10	<0.10	<0.10
	Crater #3 at 2 m	24.6	<0.01	<0.10	<0.10	<0.10	<0.10	<0.10
	Crater #4 at 1 m	1860	<0.01	<1.0	<1.0	<1.0	<1.0	<1.0
	Crater #4 at 2 m	3720	<0.01	<1.0	<1.0	<1.0	<1.0	<1.0
	Crater #4 at 5 m	2540	<0.01	<1.0	<1.0	<1.0	<1.0	<1.0
Fort Carson, CO	**25-m × 25-m area with HE chunks**	15.3	<0.01	<0.01	1.8	1.7	0.04	0.14
29 Palms, CA	**100-m × 100-m area with H-6 chunks**	1.4	9.4	1.3	<0.10	<0.10	<0.10	<0.10

* Area with chunks from 2000-lb low order

† Area away from 2000-lb low order

a Ampleman et al. 2003

b Ampleman et al. 2004

c Pennington et al. 2002

d Jenkins et al. in press

Similarly, concentrations of TNT ranged from 0.58 to 5.94 mg/kg in two 100-m × 100-m grids at HAFB, one containing an area with a low-order 2000-lb bomb and one about 50 m from the bomb. Concentrations of RDX were less than 0.1 mg/kg in most samples from this range. The concentration of TNT within a crater containing a low-order bomb averaged 60 mg/kg and the concentration within a 10-m × 10-m grid located just uphill from the crater averaged 16.1 mg/kg. Very different results were found for a 500-lb bomb crater that we sampled at Fort Polk. No energetic residues were detectable in soil samples from this crater, indicating that it was formed by a high-order detonation.

Explosives residues were detected in all of the samples collected near the target array located 2 km downstream from the Delta Creek Impact Area at Donnelly Training Area, Alaska (Walsh et al. 2004). In the composite samples, the following residues were determined: TNT (<1–314,000 µg/kg); RDX (7–1,400 µg/kg); HMX (<25–110 µg/kg); 2,4-DNT (1–33 µg/kg),and NG (<15–51 µg/kg). Only four of the samples had TNT above 1,000 µg/kg, and the median concentration was 80 µg/kg. The amino-DNT reduction products were detected in each sample as well, but concentrations were low (<200 µg/kg). One of the discrete samples collected near a 500-lb bomb partial detonation had a TNT concentration of 17,300,000 µg/kg, a concentration far exceeding any other sample we collected.

At Fort Carson, soil samples were collected in a 25-m × 25-m area where a large number of chunks of tritonal were observed on the surface. These chunks were probably deposited from a low-order bomb. The mean TNT concentration within this area was 15.3 mg/kg; TNT transformation products TNB, 2ADNT, and 4ADNT were detectable at low concentrations as well. Chunks of explosive were not included in the soil samples. Here again, the concentration of RDX was less than 0.1 mg/kg.

The H-6 explosive from a low-order bomb was detected only at 29 Palms. In this area we observed chunks of H-6 and the mean concentrations of RDX, TNT, and HMX in a 100-m × 100-m area just downslope of where the largest mass of explosive was observed were 9.4, 1.4, and 1.3 mg/kg, respectively. RDX was detected on a bombing range only where H-6 bombs were detonated, or when blow-in-place with C4 had occurred. TNT was the major energetic residue present at live-fire bombing ranges.

Demolition ranges

Demolition ranges at active DoD training facilities are used by the military explosive ordnance disposal (EOD) technicians to destroy duds of various munitions that are considered safe to move. Sometimes chunks of high explosive or

unused propellants are also destroyed at these ranges, either by demolition or burning. Demolition ranges are generally only a few hectares in size and sparsely vegetated near demolition craters. Demolition craters are often used many times before being filled in. At active installations, a quantity of C4 explosive is usually placed on the item, and it is detonated using a blasting cap, eliminating any detonation hazards from these items. Results from studies reported by Pennington et al. (2004) indicate that substantial residues of energetic compounds can sometimes be deposited during demolition events, particularly if they result in a low-order detonation for the item being destroyed or if the C4 doesn't detonate completely.

At some Air Force demolition ranges, C4 explosive is used to blow a hole in practice bombs to ensure that they contain no high explosives before these items can be removed from the range for recycling. We sampled two areas where this practice was employed, one at Eglin Air Force Base (AFB), Florida, and the other at Holloman AFB, New Mexico. Surface soil samples from both demolition ranges contain detectable concentrations of RDX and HMX (Table 14). At Eglin, the mean concentrations for six discrete samples were 8.84 and 0.54 mg/kg for RDX and HMX, respectively. At Holloman, the mean concentrations of RDX and HMX for three 30-increment composite samples collected within a 25-m circle around the demolition crater were 11.4 and 1.84 mg/kg, respectively. Because the items being detonated do not contain any explosives or propellants, the residues deposited originate from the C4 demolition explosive. The C4 demolition explosive is unconfined and this may lead to lower destruction efficiencies than for detonation of confined charges. Unconfined charges lead to detonations of lower pressure and temperature, two parameters that influence strongly the efficiency of the transformation processes in the detonation fire ball. Lower pressure and temperature cause incomplete oxidation processes and result in spreading of higher levels of unaltered energetic compounds in the environment.

Surface soil sampling was also conducted at a number of other demolition ranges at Fort Polk, Louisiana; Schofield Barracks and Pohakuloa, Hawaii; CFB-Petawawa, Ontario; Cold Lake Air Weapons Range, Alberta; and Camp Shelby, Mississippi (Table 15). These ranges were used to destroy high-explosives-containing munition items containing a variety of explosives. With the exception of two samples from CLAWR, RDX and HMX were detected in all samples from these ranges, probably from the C4 demolition explosive. Concentrations of these two explosives varied significantly from <0.03 at CLAWR to 60.2 mg/kg at Pohakuloa. At several ranges we observed pieces of C4 on the surface. During a blow-in-place test at Redstone Arsenal, small pieces of undetonated C4 were deposited over a small area when one of the two blasting caps failed and the secondary did not completely detonate the C4 block (Pennington et al. 2005).

These events probably occur infrequently, but they are probably a source of the RDX residues in some cases.

Table 14. Concentrations of explosives residues in soils at ranges where C4 was used to demonstrate that practice bombs contain no high explosive prior to metals recycling.

Installation	Date sampled	Sample#	Concentration (mg/kg)	
			HMX	RDX
Eglin AFB	Feb 03	1	0.18	1.81
		2	<0.01	0.48
		3	0.52	1.60
		4	<0.01	0.58
		5	0.61	13.9
		6	1.94	34.6
		mean	0.54	8.84
Holloman AFB	May 05	1	0.59	2.04
		2	3.98	27.8
		3	0.96	4.39
		mean	1.84	11.4

TNT was also detected in some samples from these demolition ranges, but except for two high-concentration samples from Pohakuloa, the concentrations of TNT were less than 0.6 mg/kg. NG and 2,4-DNT were detected in samples from several of these ranges. These compounds are generally components of propellant formulations where excess propellant is supposed to be destroyed by burning. Sometimes, however, these propellants are detonated instead, spreading propellant grains across the surface. It is not possible to determine whether the residues of NG and 2,4-DNT found at these ranges were from burned propellant or propellant that was incorrectly detonated.

Residue mobility

To investigate the mobility of energetic residues in the soil, we collected soil samples at depth below several low-order detonations at a variety of ranges (Table 16). The highest concentrations of TNT, RDX, or HMX were in the surface soil. Sometimes the highest concentrations for 4ADNT and 2ADNT were found in subsurface samples because these compounds are formed as dissolved TNT moves through the soil. In several of these data sets, HMX and RDX penetrated deeper into the soil profile than TNT. This is consistent with the lower soil/water partition coefficients for HMX and RDX relative to TNT (Pennington

and Brannon 2002), and the susceptibility of TNT to attenuation reactions with soil components (Haderlein et al. 1996, Thorn et al. 2002). RDX and HMX have been found in groundwater below several training ranges (Jenkins et al. 2001, Clausen et al. 2004, Mailloux et al. in press), but TNT has not.

At Fort Bliss (Pennington et al. 2003) we took a series of surface soil samples downslope from low-order detonations of a 90-mm and a 155-mm round (Table 17). In both cases some migration of energetic compounds was observed. Residues of HMX and RDX were considerably more mobile than TNT downslope of the 90-mm round. Residues of TNT were higher than RDX downslope of the 155-mm round because this round contained TNT.

Detonation craters and UXO presence

We collected a series of samples at several installations to determine the residual concentrations of energetic compounds within impact craters and around their perimeter (Table 18). RDX, HMX, TNT, 2ADNT, and NG were detected in only 46, 6, 30, 48, and 6 of the 126 samples analyzed, respectively. Except for two samples, concentrations were always less than 1 mg/kg. Similarly, we collected samples next to intact UXO items at Camp Guernsey (Table 18). Here again, residue concentrations were always below 1 mg/kg. When these UXO items at Camp Guernsey were detonated with C4 and soil samples collected in the area where the UXO item had been prior to its destruction, much higher residue concentrations were found in two of the three cases (Table 18). Overall, areas near detonation craters and intact UXO items are not heavily contaminated with residues of energetic compounds, but the destruction of UXO items with C4 (BIP) can sometimes result in a substantial increase of energetic compound concentrations in the near vicinity where the detonations occur. The use of C4 for blow-in-place detonations eliminates the safety issues associated with the presence of the UXO at training ranges; however, it can contribute to the environmental impact by distributing RDX in the environment.

Table 15. Concentrations of explosives residues in surface soils at demolition ranges where C4 was used to detonate high-explosives-containing munition items.

Installation	Date	Type*	Concentration (mg/kg)							
			HMX	RDX	TNT	4ADNT	2ADNT	2,4-DNT	NG	TNB
Cold Lake Air Weapons Range, AB	Aug 02	MI-30	<0.03	<0.03	0.01	<0.01	<0.01	<0.01	0.02	<0.01
		MI-30	<0.03	<0.03	0.52	<0.01	<0.01	<0.01	0.01	<0.01
		MI-30	<0.03	0.82	0.07	<0.01	<0.01	<0.01	<0.02	<0.01
Schofield Barrracks, HI	Nov 02	MI-30	0.70	3.94	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
		MI-30	0.68	4.38	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pohakuloa, HI	Nov 02	MI-30	7.12	39.6	0.20	0.12	0.11	<0.01	<0.01	0.06
		MI-30	7.12	45.6	9.22	0.17	0.20	<0.01	1.23	0.30
		MI-30	11.1	60.2	0.58	0.15	0.14	0.34	0.10	0.19
		MI-30	7.8	36.0	11.6	0.25	0.35	0.64	10.5	0.23
Fort Polk, LA	Jun 03	MI-30	0.03	0.17	0.03	0.02	<0.01	1.51	0.13	<0.01
		MI-30	0.07	0.33	0.09	0.08	0.13	2.4	<0.01	<0.01
CFB-Petawawa, ON	Oct 04	MI-?	1.06	30.5	<0.01	<0.01	<0.01	12.0	1.15	<0.01
		MI-?	0.08	0.72	0.05	<0.01	<0.01	2.05	0.44	<0.01
		MI-?	0.55	2.45	0.05	<0.01	<0.01	1.00	<0.01	<0.01
Camp Shelby, MS	Apr 05	MI-65	0.32	1.1	<0.04	<0.08	<0.08	<0.04	<0.1	<0.01
		MI-65	0.27	0.59	<0.04	<0.08	<0.08	<0.04	0.33	<0.01
		MI-90	0.10	0.32	<0.04	<0.08	<0.08	0.66	<0.1	<0.01

* MI: Multi-increment sample—number of increments

Table 16. Concentrations with depth samples collected below low-order (partial) detonations or chunks of explosive at artillery ranges.

Installation (location of samples)	Mean concentration (mg/kg)							
	Depth (cm)	HMX	RDX	TNT	4ADNT	2ADNT	TNB	2,4-DNT
Fort Greely, AK (under 2.75-in. warhead)	surface	40	340	130	1.0	0.84	0.17	0.036
	2–5	0.61	2.4	0.28	0.065	0.084	<0.001	<0.001
	5–7	0.06	0.38	0.013	0.015	0.024	<0.001	<0.001
	10	0.03	0.03	<0.001	0.003	0.007	<0.001	<0.001
Fort Bliss, NM (under chunk of TNT)	Surface	<1	<1	2100	<1	<1	42	<1
	1–2	<1	<1	194	<1	<1	21	<1
	2–3	<1	<1	103	<1	<1	5.4	<1
Fort Bliss, NM (under 2.75-in. warhead)	Surface	302	1,130	13.5	3.3	2.8	0.09	<0.01
	3–4	17	111	1.5	1.2	1.9	<0.01	<0.01
Fort Lewis, WA (under 155-mm round)	Surface	<0.01	<0.01	15,100	110	102	15	40
	5	<0.01	<0.01	710	146	153	<0.01	10
	10	<0.01	<0.01	46	20	30	0.14	20
	15	<0.01	<0.01	2.5	0.19	0.19	0.06	0.01
Camp Guernsey, WY (under ruptured bomb)	Surface	<10	<10	9,440	<10	<10	<10	<10
	1–3	4.2	0.6	240	<10	<10	3.2	<1
	4–7	1.3	<1	42	14.9	19	0.96	2.0
Fort Hood, TX (under low-order 81-mm mortar)	Surface	52	212	5.0	6.5	8	<0.01	0.76
	1–3	6.3	26	0.48	2.2	3	<0.01	0.23
	3–7.5	6.7	26	1.6	1.7	3.2	<0.01	0.18
	7.5–10	4.2	13	0.30	1.1	2.0	<0.01	0.14
Fort Hood, TX (under chunk of Composition B)	Surface	129	861	459	14	9.8	<0.01	<0.01
	1–4	31	173	31	8.7	5.1	<0.01	<0.01
	9–14	127	832	331	2.8	1.9	<0.01	<0.01
	16–20	12	56	9.5	2.2	1.4	<0.01	<0.01

Table 16 (cont'd). Concentrations with depth samples collected below low-order (partial) detonations or chunks of explosive at artillery ranges.

Installation (location of samples)	Mean concentration (mg/kg)							
	Depth (cm)	HMX	RDX	TNT	4ADNT	2ADNT	TNB	2,4-DNT
Fort Hood, TX (area with Composition B)*	Surface	0.95	2.2	0.064	0.21	0.24	<0.001	<0.001
	2–6	0.40	3.7	<0.001	<0.001	<0.001	<0.001	<0.001
	6–9	0.12	0.33	<0.001	<0.001	<0.001	<0.001	<0.001
	9–12	0.13	0.25	<0.001	<0.001	<0.001	<0.001	<0.001
	12–16	0.10	0.22	<0.001	<0.001	<0.001	<0.001	<0.001
Fort Carson, CO (under 106-mm HEP round)	Surface	59	336	<0.01	<0.01	<0.01	<0.01	<0.01
	3–4	19	97	<0.01	<0.01	<0.01	<0.01	<0.01
	4–5	8.9	49	<0.01	<0.01	<0.01	<0.01	<0.01
	5–6	1.3	5.8	<0.01	<0.01	<0.01	<0.01	<0.01
	6–7	1.1	4.6	<0.01	<0.01	<0.01	<0.01	<0.01
	7–8	1.4	6.0	<0.01	<0.01	<0.01	<0.01	<0.01

* No chunks present at surface

Table 17. Concentration of energetic compounds for soil samples collected downslope of low-order (partial) detonations or chunks of explosive at Fort Bliss.

Installation (location of samples)	Down-slope (m)	Mean concentration (mg/kg)						
		HMX	RDX	TNT	4ADNT	2ADNT	TNB	2,4-DNT
Fort Bliss, NM (low-order 155-mm with chunks of TNT)*	0.2	<0.03	<0.03	6,270	<0.03	<0.04	98	<0.003
	1	<0.03	<0.03	1.3	0.2	0.17	<0.02	<0.003
	2	<0.03	<0.03	38	0.8	0.07	<0.02	<0.003
	3	<0.03	0.05	0.01	<0.002	<0.003	<0.003	<0.003
	4	<0.03	0.10	0.03	0.003	<0.003	<0.003	<0.003
	5	<0.03	0.02	348	0.007	0.004	<0.003	<0.003
	12	0.04	0.03	0.04	<0.002	<0.003	<0.003	<0.003
	30	<0.03	<0.003	<0.001	<0.002	<0.003	<0.003	<0.003
Fort Bliss, NM (low-order 90-mm)	0	149	678	1,100	12	18	9.0	1.3
	2	50	110	0.38	0.15	0.10	0.09	0.04
	3.7	41	39	0.21	0.12	0.06	<0.001	<0.001
	6	3.3	0.67	<0.001	<0.001	<0.001	<0.001	<0.001

* 155-mm round located in an arroyo

Table 18. Summary of concentrations for energetic compounds (mg/kg) for crater samples and samples next to intact UXO items at artillery ranges in the United States and Canada.

Installation	Year sampled	Crater samples analyzed	Type of craters	HMX		RDX		TNT		2ADNT		NG	
				Number <d[†]	Max value	Number <d	Max value	Number <d	Max value	Number <d	Max value	Number <d	Max value
Fort Greely (Donnelly Training Area), AK	2000	3 craters (13 samples)	BIP* mortar, tow missile, SADARM	13	<0.026	5	0.016	6	0.008	12	0.003	12	0.37
Fort Lewis, WA	2000	12 craters (47 samples)	Live-fire , mortars, artillery	47	<0.026	30	0.093	28	1.75	16	0.031	ND*	ND
Yakima Training Center, WA	2001	5 craters (31 samples)	Live fire, artillery	31	<0.026	26	0.017	31	<0.001	30	0.003	31	<0.022
CFB-Gagetown, New Brunswick	2002	8 craters (15 samples)	artillery	13	1.1	11	6.4	11	1.9	8	0.14	11	0.12
Fort Polk, LA	2003	5 craters (15 samples)	105-mm, 155-mm, bombs	14	0.060	4	0.061	12	0.27	11	0.46	13	0.005
Schofield Barracks, HI	2003	5 craters (8 samples)		8	<0.026	4	0.015	8	<0.001	1	0.013	8	<0.022
Camp Guernsey, WY	2001	36	three 155-mm rounds	21	0.53	18	0.33	13	0.550	4	0.45	36	<0.022
Yakima Training Center, WA	2001	10	105-mm, 155-mm, illumination	9	0.026	7	0.72	10	<0.001	8	0.049	10	<0.022
Camp Guernsey, WY	2001	49	three 155-mm rounds	11	83	11	541	7	294	26	0.59	49	<0.022

* BIP: Blow-in-place detonation crater

[†] Number of samples where concentrations were below analytical detection limits

4 SUMMARY AND CONCLUSIONS

The types of residues, their concentrations, and distributions differ depending on the type of range and munition used. In general, the largest residue concentrations for all impact areas appear to be due to low-order detonations spreading particles and larger chunks of high explosive over the soil surface.

For hand grenade ranges, low-order detonations occur either when grenades are thrown during training or when duds are blown in place using C4 explosive. The C4 explosive used for detonating duds contains 91% military-grade RDX, of which about 10% is HMX. The major energetic residues on hand grenade ranges are RDX and TNT from Composition B, the explosive charge in M67 and C13 fragmentation grenades. For ranges where a recent partial detonation has occurred, concentrations are generally in the low mg/kg range and the distributions are more spatially homogeneous than at other types of impact ranges due to the thousands of individual detonations that continually redistribute the residue. Because grenade ranges are small in size, composite samples consisting of 30 increments have been found to be adequate for obtaining representative samples of surface soils.

At antitank rocket ranges the major residue present in surface soils at the target area is HMX from the octol used as the high explosive in the warhead of 66-mm M72 LAW rockets. A concentration gradient is present in surface soils relative to the distance from targets. HMX concentrations in surface soils near targets are generally in the hundreds to low thousands of mg/kg, with TNT concentrations about one-hundredth that of HMX. The high levels of HMX in the soil at antitank rocket ranges can be attributed to the high dud- and rupture rate of the M72 rockets. For sample collection, the impact area should be stratified into areas near targets, and areas in front of and in back of targets. Short-range spatial heterogeneity in residue concentrations at these sites is high, and in order to get representative samples, it is necessary to take multi-increment samples with a minimum of 30 increments.

At the firing points of antitank rocket ranges, NG is present from the double-base propellant used in the 66-mm M72 rockets. The major deposition of residue is behind the firing line due to the back blast from this weapon. Concentrations as high as the low percent level are sometimes found in soil up to 25 m behind the firing line. NG is also found between the firing line and the target, but the concentrations are generally several orders of magnitude lower than behind the firing line. Multi-increment samples have been found to provide adequate characterization for samples from impact areas and firing points at antitank rocket ranges.

Because the residues in these samples are largely present as particles of propellant, samples must be processed using larger sieves (10 mesh, 2 mm) than recommended in SW846 Methods 8330 and 8095. We also recommend thorough grinding of samples using a mechanical grinder prior to subsampling to preserve the representativeness of the portion of the sample to be used for extraction and analysis.

Most of the total acreage at artillery ranges that is remote to firing points and targets is uncontaminated with residues of energetic compounds. At artillery and mortar firing points, the energetic residues are usually either 2,4-DNT or NG, depending on the type of propellant used for the specific firing platform. Residues can be deposited at distances up to 100 meters in front of the muzzle. For 105-mm howitzers, the major detectable residue is 2,4-DNT, which can accumulate into the mg/kg range for fixed firing points. The residues from the single-base propellant used with this weapon are distributed primarily as burnt or unburnt propellant fibers. Residue deposition from 155-mm howitzers and mortars is primarily NG from double- or triple-base propellants. The NG does not seem to accumulate to concentrations as high as those for 2,4-DNT from single-base propellants. Propellant residues are deposited at the soil surface and the highest concentrations remain at the surface unless the soil is disturbed. Both NG and 2,4-DNT are deposited in an NC fiber matrix, thereby probably limiting their bioavailability and leachability.

Near targets at impact ranges, the majority of detonations of munitions are high-order detonations, and, as found by Hewitt et al. (2003), they appear to deposit very little residue. The major energetic residue deposition is due to low-order (partial) detonations that can deposit chunks of pure explosive. Residue concentrations of hundreds or thousands of mg/kg are often found in the surface soils next to these detonations. The major residues are TNT and RDX from military-grade TNT and Composition B, the major explosives used in mortar and artillery rounds. The distribution of residues in the area of the range where detonations occur is best described as randomly distributed point sources. Some of these point sources may be due to low-order detonations that are from blow-in-place of surface UXO items. At present the detection of these point source areas has been visual, but research is underway to try to develop a near-real time detection capability. The collection of representative samples in areas subject to these partial detonations is a major challenge and approaches utilizing multi-increment sampling have not been adequate.

The major residue present at bombing ranges is generally TNT from the tritonal used as the high explosive in most bombs. Concentrations can be in the tens to hundreds of ppm in and near bomb craters where low-order detonations

have occurred. RDX concentrations are generally low at these ranges unless a bomb containing H-6 explosive had undergone a low-order detonation.

RDX and HMX from C4 are generally the residues present at highest concentrations in demolition ranges where C4 explosive is used to blast small holes in practice bombs to ensure that they contain no high explosive prior to recycling activities. RDX is generally the residue present at the highest concentration at EOD demolition ranges due to use of C4 to destroy duds and other explosives-containing items. Concentrations can sometimes be in the low mg/kg in surface soils at these sites.

RDX and HMX appear to be the most mobile of the energetic compounds present at training ranges. This is true for both downward migration through the soil profile and also overland in runoff. This agrees with results reported for energetic compounds in groundwater (Clausen et al. 2004, Jenkins et al. 2001).

Results of these studies demonstrate that the potential for range contamination is specific to the type of range and the type of activity. Large areas of training ranges are uncontaminated, while residues in smaller areas, e.g., those around targets, firing points, and low-order detonations, are potentially significant. Range managers can, therefore, limit management practices for residue control to specific areas and specific types of firing activities.

REFERENCES

Ampleman, G., S. Thiboutot, J. Lewis, A. Marois, S. Jean, A. Gagnon, M. Bouchard, T.F. Jenkins, J.C. Pennington, and T.A. Ranney (2003a) Evaluation of the contamination by explosives in soils, biomass and surface water at Cold Lake Air Weapons Range (CLAWR), Alberta, Phase 1 Report. Defence Research Development Canada-Valcartier, Technical Report TR 2003-208.

Ampleman, G., S. Thiboutot, J. Lewis, A. Marois, A. Gagnon, M. Bouchard, R. Martel, R. Lefebvre, T.A. Ranney, T.F. Jenkins, and J.C. Pennington (2003b) Evaluation of the impacts of live-fire training at CFB Shilo (Final Report). Defence Research Development Canada-Valcartier, Technical Report TR 2003-066.

Ampleman, G., S. Thiboutot, J. Lewis, A. Marois, A. Gagnon, M. Bouchard, T. Jenkins, T.A. Ranney, and J.C. Pennington (2004) Evaluation of the contamination by explosives and metals in soils, vegetation, surface water, and sediment at Cold Lake Air Weapons Range (CLAWR), Alberta, Phase II Final Report. DRDC-Valcartier Technical Report 2004-204.

Clausen, J., J. Robb, D. Curry, and N. Korte (2004) A case study of contaminants on military ranges: Camp Edwards, Massachusetts, USA. *Environmental Pollution*, **129**: 13–21.

Dube, R., G. Ampleman, S. Thiboutot, A. Gagnon, and A. Marois (1999) Chacterization of potentially explosives-contaminated sites at CFB-Gagetown, 14 Wing Greenwood and CFAD Bedford. Defence Research Establishment Valcartier, Quebec Report # DREV–TR-1999-137.

Environmental Protection Agency (1994) Nitroaromatics and Nitramines by HPLC, Second Update SW846 Method 8330.

Environmental Protection Agency (1999) Nitroaromatics and Nitramines by GC-ECD, Fourth Update SW846 Method 8095.

Haderlein, S.B., K.W. Weissmahr, and R.P. Schwarzenbach (1996) Specific adsorption of nitroaromatic explosives and pesticides to clay minerals, *Environmental Science and Technology*, **30**: 612–622.

Hewitt, A.D., T.F. Jenkins, T.A. Ranney, J.A. Stark, M.E. Walsh, S. Taylor, M.R. Walsh, D.J. Lambert, N.M. Perron, N.H. Collins, and R. Karn (2003) Estimates for explosives residues from the detonation of Army munitions. U.S. Army Engineer Research and Development Center, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-03-16.

Hewitt, A.D., T.F. Jenkins, T.A. Ranney, D. Lambert, and N. Perron (2004) Chapter 3 in Pennington, J.C., T.F. Jenkins et al. (2004): Distribution and fate of energetics on DoD test and training ranges, ERDC Interim Report. U.S. Army Engineer Research and Development Center, Vicksburg, Mississippi, Technical Report ERDC TR-04-4.

Hewitt, A.D., T.F. Jenkins, C.A. Ramsey, K.L. Bjella, T.A. Ranney, and N. Perron (2005) Estimating energetic residue loading on military artillery ranges: Large decision units. U.S. Army Engineer Research and Development Center, Hanover, New Hampshire, Technical Report, ERDC/CRREL TR-05-7.

Jenkins, T.F., M.E. Walsh, P.G. Thorne, S. Thiboutot, G. Ampleman, T.A. Ranney, and C.L. Grant (1997) Assessment of sampling error associated with the collection and analysis of soil samples at a firing range contaminated with HMX. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Special Report 97-22.

Jenkins, T.F., M.E. Walsh, P.G. Thorne, P.H. Miyares, T.A. Ranney, C.L. Grant, and J. Esparza (1998) Site characterization for explosives at a military firing range impact area. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Special Report 98-9.

Jenkins, T.F., C.L. Grant, M.E. Walsh, P.G. Thorne, S. Thiboutot, G. Ampleman, and T.A. Ranney (1999) Coping with spatial heterogeneity effects on sampling and analysis at an HMX-contaminated antitank firing range. *Field Analytical Chemistry and Technology*, **3**(1): 19–28.

Jenkins, T.F., J.C. Pennington, T.A. Ranney, T.E. Berry, Jr., P.H. Miyares, M.E. Walsh, A.D. Hewitt, N. Perron, L.V. Parker, C.A. Hayes, and E. Wahlgren (2001) Characterization of explosives contamination at military firing ranges. U.S. Army Engineer Research and Development Center, Hanover, New Hampshire, Technical Report ERDC TR-01-05.

Jenkins, T.F., T.A. Ranney, A.D. Hewitt, M.E. Walsh, and K.L. Bjella (2004a) Representative sampling for energetic compounds at an antitank firing range. U.S. Army Engineer Research and Development Center, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-04-7.

Jenkins, T.F., T.A. Ranney, A.D. Hewitt, C.A. Ramsey, D. Lambert, K.L. Bjella, and N. Perron (2004b) Sampling strategies near a low-order detonation and a target at an antitank impact area. U.S. Army Engineer Research and Development Center, Hanover, New Hampshire, ERDC/CRREL Technical Report 04-14.

Jenkins, T.F., A.D. Hewitt, M.E. Walsh, T.A. Ranney, C.A. Ramsey, C.L. Grant, and K.L. Bjella (2005) Representative sampling for energetic compounds at military training ranges. *Environmental Forensics*, 6: 45–55.

Jenkins, T.F., A.D. Hewitt, C.A. Ramsey, S.R. Bigl, Kevin Bjella, and D. Lambert (in press) Sampling studies at an Air Force bombing range impact area. U.S. Army Engineer Research and Development Center, Hanover, New Hampshire, ERDC Technical Report.

Leggett, D.C., T.F. Jenkins, and R.P. Murrmann (1977) Composition of vapors evolved from military TNT as influenced by temperature, solid composition, age, and source. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Special Report 77-16.

Lewis, J.K. (2004) An investigation of the fate and transport of Composition B and detonation residues originating from cracked unexploded ordnance in unsaturated soil. Ph.D. thesis, Institut National de la Recherche Scientifique–Centre Eau, Terre & Environnement, Québec, Quebec, Canada.

Mailloux, M., R. Martel, R. Lefebvre, G. Ampleman, and S. Thiboutot (2000) Energetic materials behaviour in groundwater at the Arnhem antitank range, CFB-Valcartier, Québec, Canada. In *Proceedings of the First Joint IAH-CNC and CGS Groundwater Specialty Conference*, Montréal, Canada, October 2000.

Mailloux, M., R. Martel, R. Lefebvre, S. Thiboutot, and G. Ampleman (in press) Behaviour of energetic materials in groundwater at an antitank range. *Journal of Groundwater, Monitoring and Remediation*.

McCormick, N.G., F.E. Feeherry, and H.S. Levinson (1976) *Applied and Environmental Microbiology*, **31**: 949–958.

Pennington, J.C., and J.M. Brannon (2002) Environmental fate of explosives. *Thermochimica Acta*, **384**: 163–172.

Pennington, J.C., T.F. Jenkins, G. Ampleman, S. Thiboutot, J.M. Brannon, J. Lynch, T.A. Ranney, J.A. Stark, M.E. Walsh, J. Lewis, C.A. Hayes, J.E. Mirecki, A.D. Hewitt, N. Perron, D. Lambert, J. Clausen, and J.J. Delfino (2002) Distribution and fate of energetics on DoD test and training ranges: Interim Report 2. U.S. Army Engineer Research and Development Center, Vicksburg, Mississippi, Technical Report ERDC TR 02-8.

Pennington, J.C., T.F. Jenkins, G. Ampleman, S. Thiboutot, J.M. Brannon, J. Lewis, J.E. Delaney, J. Clausen, A.D. Hewitt, M.A. Hollander, C.A. Hayes, J.A. Stark, A. Marois, S. Brochu, H.Q. Dinh, D. Lambert, A. Gagnon, M. Bouchard, R. Martel, P. Brousseau, T.A. Ranney, C. Gauthier, S. Taylor, and J.M. Ballard (2003) Distribution and fate of energetics on DoD test and training ranges: Interim Report 3. U.S. Army Engineer Research and Development Center, Vicksburg, Mississippi, Technical Report ERDC TR-03-2.

Pennington, J.C., T.F. Jenkins, G. Ampleman, S. Thiboutot, J.M. Brannon, J. Lewis, J.E. Delaney, J. Clausen, A.D. Hewitt, et al. (2004) Distribution and fate of energetics on DoD test and training ranges: Interim Report 4. U.S. Army Engineer Research and Development Center, Vicksburg, Mississippi, Technical Report ERDC TR-04-4.

Pennington, J.C., T.F. Jenkins, et al. (2005) Distribution and fate of energetics on DoD test and training ranges: Interim Report 5. U.S. Army Engineer Research and Development Center, Vicksburg, Mississippi, Technical Report ERDC TR-05-2.

Pitard, F. (1993) *Pierre Gy's Sampling Theory and Sampling Practice, 2nd Edition*. Boca Raton, Florida: CRC Press.

Taylor, S., A. Hewitt, J. Lever, C. Hayes, L. Perovich, P. Thorne, and C. Daghlian (2004) TNT particle size distributions from detonated 155-mm howitzer rounds. *Chemosphere*, **55**: 357–367.

Thiboutot, S., G. Ampleman, A. Gagnon, A. Marois, T.F. Jenkins, M.E. Walsh, P.G. Thorne, and T.A. Ranney (1998) Characterization of antitank firing ranges at CFB Valcartier, WATC Wainwright and CFAD Dundurn. Defence Research Establishment Valcartier, Quebec Report # DREV-R-9809.

Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, M. Bouchard, A. Hewitt, T. Jenkins, M. Walsh, and K. Bjella (2003) Environmental condition of surface soils and biomass prevailing in the training area at CFB Gagetown, New Brunswick. Defence Research and Development Canada Valcartier, DRDC Valcartier TR 2003-152.

Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, M. Bouchard, A. Hewitt, T. Jenkins, M. Walsh, and K. Bjella (2004) Environmental condition of surface soils, CFB Gagetown Training Area: Delineation of the presence of munitions-related residues (Phase III, Final Report). Defence Research and Development Canada Valcartier, DRDC Valcartier TR 2004-205.

Thorn, K.A., J.C. Pennington, and C.A. Hayes (2002) 15N NMR investigations of the reduction and binding of TNT in an aerobic bench scale reactor simulating windrow composting. *Environmental Science and Technology*, **36**: 3739–3805.

USACHPPM (2001) Final Geohydrologic Study No. 38-EH-8879-99, Training range site characterization and risk screening, Camp Shelby, Mississippi, 7–23 September 1999.

USACHPPM (2003) Project No. 38-EH-8220-03, Training range site characterization and risk screening, regional range study, Jefferson Proving Ground, Madison, Indiana, September 2002.

USACHPPM (2004) Geohydrologic Study No. 38-EH-6807-02, Training range site characterization and risk screening, regional range study, Dona Ana Range, Fort Bliss, Texas, May 2002.

USACHPPM (in press) Project No. 38-EH-00M2-04, Training range site characterization and risk assessment, regional range study, Redleg Impact Area, Fort Polk, Louisiana, March 2005.

Walsh, M.E., C.M. Collins, and C.H. Racine (1995**)** Persistence of white phosphorus particles in sediment. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, CRREL Report 95-23.

Walsh, M.E., C.M. Collins, R.N. Bailey, and C.L. Grant (1997**)** Composite sampling of sediments contaminated with white phosphorus. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Special Report 97-30.

Walsh, M.E., C.M. Collins, C.H. Racine, T.F. Jenkins, A.B. Gelvin, and T.A. Ranney (2001) Sampling for explosives residues at Fort Greely, Alaska: Reconnaissance visit July 2000. U.S. Army Engineer Research and Development Center, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-01-15.

Walsh, M.E., C.A. Ramsey, and T.F. Jenkins (2002) The effect of particle size reduction by grinding on subsampling variance for explosives in soil. *Chemosphere*, **49**: 1267–1273.

Walsh, M.E., C.M. Collins, A.D. Hewitt, M.R. Walsh, T.F. Jenkins, J. Stark, A. Gelvin, T. Douglas, N. Perron, D. Lambert, R. Bailey, and K. Myers (2004) Range characterization studies at Donnelly Training Area, Alaska 2001 and 2002. U.S. Army Engineer Research and Development Center, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-04-3.

Walsh, M.E., C.A. Ramsey, C.M. Collins, A.D. Hewitt, M.R. Walsh, K.L. Bjella, D.J. Lambert, and N.M. Perron (2005) Collection methods and laboratory processing of samples from Donnelly Training Area firing points, Alaska, 2003. U.S. Army Engineer Research and Development Center, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-05-6.

Walsh, M.R. (2004) Field sampling tools for explosives residues developed at CRREL. U.S. Army Engineer Research and Development Center, Hanover, New Hampshire, Technical Note ERDC/CRREL TN 04-1.

Walsh, M.R., M.E. Walsh, T.F. Jenkins, A.D. Hewitt, and C.A. Ramsey (2005) Optimization of explosives residues collection from the detonation of munitions on snow-covered ice. U.S. Army Engineer Research and Development Center, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-05-8.

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14. ABSTRACT

Environmental stewardship of military training ranges is an important objective of the Department of Defense. Therefore, an understanding of the explosives residues resulting from military training with various weapon systems is critical to range managers. A series of field sampling experiments was conducted at 27 military firing ranges in the United States and Canada to provide information on the identity and distribution of energetic munitions constituents. Different types of ranges were studied, including hand grenade, antitank rocket, artillery, bombing, and demolition ranges. Both firing points and impact areas were studied. Energetic compounds (explosives and propellants) were determined and linked to the type of munition used and the major mechanisms of deposition. At impact areas, the largest deposition of residues of energetic compounds is due to low-order detonations, or, in some cases, munitions that split open upon impact. The major residue deposited and its distribution varies for different types of ranges based upon the composition of the high explosive present in the warheads of the rounds fired at that type of range. For antitank range impact areas, the major residue present is HMX from the octol explosive used in the M72 66-mm LAW rockets. At artillery range impact areas, the major residues are TNT and/or RDX from the military-grade TNT and Composition B used in warheads of artillery and mortar rounds. Residues are very heterogeneously distributed at artillery range impact areas

(continued)

15. SUBJECT TERMS

2,4-DNT	Demolition ranges	Hand grenade ranges	Nitroglycerin	Training ranges
Antitank ranges	Energetic compounds	HMX	Propellants	
Artillery ranges	Explosives	Impact areas	RDX	
Bombing ranges	Firing points	Live fire	TNT	

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ABSTRACT ***(continued)***

and can be described as randomly distributed point sources. RDX and TNT are the major residues at hand grenade ranges and their distribution is less heterogeneous due to the large number of individual detonations in a smaller area that further disperses the residues over the surface and at shallow depths. TNT is the major energetic compound detected at bombing ranges due to its presence in tritonal, the most common explosive used in bombs. RDX is the most common energetic compound at demolition ranges due to its presence as the major component of C4 demolition explosive. NG and 2,4-DNT are also frequently detected at demolition ranges as a result of the disposal of excess propellant. Once dissolved, RDX and HMX are the most mobile of the organic energetic compounds deposited on ranges, both vertically in the soil profile and horizontally across the surface.

Results of these studies demonstrate that the potential for range contamination is specific to range activities. Large areas of training ranges are uncontaminated, while residues in smaller areas, e.g., those around targets, firing points, and low-order detonations, are potentially significant. Range managers can, therefore, limit management practices for residue control to specific areas and specific types of firing activities.